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Removal of lanthanum, cerium, europium and holmium from water by co-precipitation with iron and aluminium (hydr)oxides

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Abstract

Effluents from mining activities may have high concentrations of trace elements such as arsenic, rare earth elements (REE) and actinides, mainly in areas where acid mine drainage (AMD) occurs. Use of lime to neutralise AMD also promote co-precipitation of iron (Fe) and aluminium (Al) (hydr)oxides, increasing the removal of trace elements from water. This study aimed to evaluate the efficiency of Fe/Al (hydr)oxides co-precipitation to remove lanthanum (La), cerium (Ce), europium (Eu) and holmium (Ho) from water under laboratory conditions. Two sets of experiments were performed with individual REE solutions containing Eu and Ho. In these cases, Fe(II) and Al sulphates were used at different Fe:Al:REE molar ratios. Two other sets of experiments with Fe(II) and Fe(III) sulphates were performed in a mixed REE solution containing La, Ce, Eu and Ho. To co-precipitate Fe/Al (hydr)oxides, pH's were raised to 9.0 and 6.0 with 5 mol L^{-1} KOH solution. Soluble contents of Fe, Al and REE were periodically measured in supernatants aliquots. Precipitates were collected at the end of the 60-day incubation period and, then, oven-dried, sieved and characterised by X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis. The stability of REE in precipitates was also assessed by BCR sequential extractions. All treatments presented high REE removal efficiency from water at pH 9.0, but significantly lower at pH 6.0 for Fe(II) treatments. Magnetite precipitation was favoured by lower contents of REE and Al, whereas goethite and lepidocrocite were favoured at higher contents. Segregated phases were not detected for Eu and Ho, but lanthanite and cerianite precipitated at high amounts of La and Ce, respectively. For mixed REE treatments, the mineralogical phases precipitated were mostly poorly crystallised. The presence of magnetite was associated to higher REE stabilities, whereas lepidocrocite decreased the stability as measured by BCR extractions. The presence of segregated phases as cerianite resulted in increased Ce stability, but presence of lanthanite decreased La stability in precipitates.

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This thesis *is composed of my original work, and contains* no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

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LIST OF ABBREVIATIONS

Al	Aluminium
AMD	Acid Mine Drainage
As	Arsenic
BCR	Bureau Communautaire de Référence
Ce	Cerium
Cn	Cerianite
Co	Cobalt
Cr	Chromium
Cu	Copper
DL	Detection Limit
Eu	Europium
Fe	Iron
Fe(II)	Ferrous Iron
Fe(III)	Ferric Iron
Fh	Ferrihydrite
Gb	Gibbsite
Gt	Goethite
Ho	Holmium
HREE	Heavy Rare Earth Elements
HRTEM	High-resolution Transmission Electron Microscopy
IBRAM	Brazilian Mining Institute
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
La	Lanthanum
Ln	Lanthanite
Lp	Lepidocrocite
LREE	Light Rare Earth Elements
MB	Mass Balance
Mn	Manganese
Mo	Molybdenum

MREE	Medium Rare Earth Elements
Mt	Magnetite
Ni	Nickel
P	Phosphorus
REE	Rare Earth Elements
REE_{FSC}	REE Final Soluble Concentrations
REE_{ISC}	REE Initial Soluble Concentrations
REE_{TCP}	REE Total Contents in Precipitates
SEM	Scanning Electron Microscopy
SEP	Sequential Extraction Procedures
USA	United States of America
V	Vanadium
XAS	X-ray Absorption Spectroscopy
XRD	X-ray diffraction

1. Introduction

The REE comprise a group of chemical elements including the lanthanide series, which begins with lanthanum (La, Z=57) and ends with lutetium (Lu, Z=71). Furthermore, two other elements are included: scandium (Sc, Z = 39) and yttrium (Y, Z = 21), chemically similar to the lanthanides. They are commonly found in the same mineral assemblages and are often considered together with the REE in geochemical investigations (EPA 2012). Most REE form stable 3+ ions with very similar chemical and physical properties. However, a small number of REE can exist in oxidation states other than 3+, but only cerium (Ce^{4+}) and europium (Eu^{2+}) are important in natural environments (Abrão 1994). REE can also be grouped according to their atomic mass as light (LREE), from La to Gd, and heavy REE (HREE), from Tb to Lu (USGS 2014). Some authors such as Voncken (2016) and Kingsnorth (2010) also add a medium class (MREE). These authors nominate La to Nd as LREE, Pm to Gd as MREE and Tb to Lu as HREE.

A characteristic phenomenon of the REE is the lanthanide contraction, which is a decrease in the atomic radius as the atomic number increases in this group. This is contrary to the general trend for other elements that present larger atomic radius as the atomic number increases, due to attachment of electrons to the outer orbitals. However, insertion of electrons in REE involves the lower-lying 4f-orbital, resulting in stronger forces inside the atoms. This peculiarity accounts for the decrease in atomic radius despite the similar outer electron appearance (Zepf 2013).

REE are found as minor or trace constituents in rocks. Some of them have atomic radius similar to rock-forming elements. For this reason, REE are often found in rocks that contain calcium, thorium, uranium, and strontium (Zepf 2013). Global REE reserves were estimated in 130 million ton by the USA Geological Service in 2014 (USGS 2015b), being 55 million ton in China (42%) and 22 million ton in Brazil (17%). Australia and USA together own 5 million ton, which is less than 5% of global reserves (USGS, 2015a). They appear in variable quantities in some minerals such as bastnaesite [(La, Ce, Y)(CO_3)F], monazite [(Ce,La,Nd,Th)PO_4], xenotime [Y(PO_4)] and apatite [$Ca_5(PO_4)_3$(OH,F,Cl)] (Rosental 2008). Bastnaesite and monazite are the most important

sources of LREE while HREE are mostly found in xenotime. Such ores typically contain 5-15% of REE in mass percentage (Jones et al. 1996). A growing source of REE is the adsorbed pool in clays (often muscovite), particularly in subtropical Asia, mainly China. Notwithstanding, REE represent only 0.2-0.3% in mass in these ores, therefore large volumes must be processed in order to recover significant amounts of these elements (Lucas et al. 2015).

In Brazil, REE deposits occur mainly in cratonic areas (primary and secondary deposits) and along the marine coast (secondary deposits). Primary deposits are related to alkaline carbonatites and granitic rocks while secondary deposits are alteration products such as clay deposits and marine placers (Takehara et al. 2016). The alkaline carbonatite complexes are more related to LREE and they are located mainly in Minas Gerais and Goiás states. On the other hand, granitic rocks are more related to HREE and the main occurrence areas are in Goiás and Amazonas states (Takehara et al. 2016).

In Minas Gerais state, Brazil, a REE-rich deposit, with an assemblage of primary and secondary minerals occurs in the Poços de Caldas municipality region (Waber 1992). Bastnaesite is the most abundant mineral followed by cerianite and thorugummite (Takehara et al. 2016). The first two are considered supergenic products (Waber 1992), therefore secondary minerals resulting from weathering processes. Concentrations of thorium (Th), uranium (U) and REE increase with increasing amounts of ferruginous clay minerals in this deposit. However, the concentrations of these elements decreases in areas containing unaltered magnetite (Takehara et al. 2016). Such reports clearly show that weathering processes are responsible for enrichment of REE associated to secondary Fe (hydr)oxides.

There are a wide range of REE applications in high-tech industry, from green technology (e.g. electric cars, wind turbines), to advanced components for electronics (e.g. lasers, mobile phones) and oil industry (e.g. catalysts), among others (Golev et al. 2014; Massari and Ruberti 2013) (Fig. 1). Due to this vast range of industrial uses, the REE commercialisation has increased along time. It started around the 1900s (Zepf 2013) with an increasing since then, reaching a production of 110,000t in 2014 (USGS 2015b).

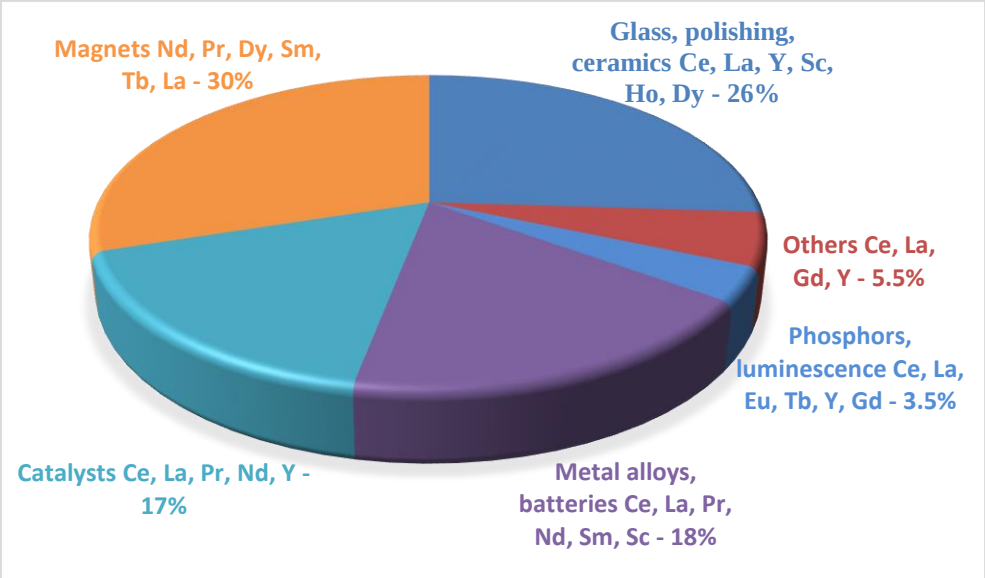

Fig. 1 Main applications of rare earth elements. Font: Golloch (2017).

Increasing exploitation of REE deposits and widespread use of REE is becoming an environmental concern mainly due to their association with other elements such as arsenic (As), Th and U. This can lead to an increase in mobility and then to contamination of soil, air and water. The problem is even more critical where the generation of acid mine drainage (AMD) is observed. The exposition of sulphide-bearing minerals to atmospheric conditions produces acidic waters (AMD) with high polluting potential (Singer and Stumm 1970). At low pH, the trace elements present in the system are mobilised and can be released into the environment causing contamination.

The driving reaction of AMD is the oxidation of pyrite, which produces sulphates, ferric (hydr)oxides and acidity (Eq. 1 to 3), according to Singer and Stumm (1970).

$$FeS_{2(s)} + 7/2\ O_{2(g)} + H_2O_{(aq)} \rightarrow Fe^{2+}_{(aq)} + 2SO_4^{2-}{}_{(aq)} + 2H^+_{(aq)} \quad (1)$$

$$Fe^{2+}_{(aq)} + 1/4O_{2(g)} + H^+_{(aq)} \rightarrow Fe^{3+}_{(aq)} + 1/2H_2O_{(aq)} \quad (2)$$

$$Fe^{3+}_{(aq)} + 3H_2O_{(aq)} \rightarrow Fe(OH)_{3(s)} + 3H^+_{(aq)} \quad (3)$$

The restraining step in abiotic system is the Fe^{2+} oxidation due to its slow rate (Eq. 2). However, at low pH (< 3) as found in AMD areas the presence of bacteria such as *Acidithiobacillus* spp. and *Leptospirillum* spp. can increase the oxidation rate up to 5 orders of magnitude (Sanchez-Andrea et al. 2014). Under such conditions, concentration of Fe^{3+} increases and it can oxidise sulphides even more effectively than oxygen

(Nordstrom et al 2015), which increases the acidity (Eq. 4) in an auto-propagating AMD cycle.

$$FeS_{2(s)} + 14Fe^{3+}_{(aq)} + 8H_2O_{(aq)} \rightarrow 15Fe^{2+}_{(aq)} + 2SO_4^{2-}{}_{(aq)} + 16H^{+}_{(aq)} \quad (4)$$

Therefore, the Fe^{2+}/Fe^{3+} equilibria is affected by the decrease in pH values. Under natural atmospheric conditions, Fe^{2+} is more soluble while Fe^{3+} mostly precipitates as Fe-(hydr)oxide. However, the concentration of Fe^{3+} in solution may remain high at low pH, thus the two oxidation states of Fe must be considered in AMD scenario.

The concern regarding AMD occurrence in Brazil is due to the presence of over 8 thousands of active mines in the country. According to the Brazilian Mining Institute (IBRAM), just in Minas Gerais state, there are over 300 active mines and some of them are among the largest mines in the country. This makes this state responsible for 53% of the metal extractions and for 29% of ore production in the country (IBRAM 2015). The Osamu Utsumi uranium mine, located about 15 km south of Poços de Caldas municipality (southwestern part of Minas Gerais state), is a typical example of high AMD generating mine. Uranium was discovered in the area in 1948, geological research commenced in 1964 and mining in 1982. This mine then became the first to produce yellow cake (concentrated of uranium) in Brazil (Nóbrega et al. 2008). The deposit is hosted in Mezozoic alkaline volcanic, subvolcanic and plutonic rocks, usually containing uranium, thorium and rare earth elements (Ulbrich 1984). The mine was closed in 1995, but the demand for acid mine drainage (AMD) treatment is still around 300 m^3/h (Nóbrega et al. 2008), so it requires on-going efforts and investment. For this reason, this mine is a good case-study for investigation of rare earth elements (REE) in mining effluents.

The development of techniques to treat the mining wastewater is needed. There are two different ways to treat AMD: through passive or active methods. Passive treatment is commonly considered when the continuous addition of alkaline chemical reagents is not required. Intensity of AMD generation, as well as the extent of the affected area and differences in operation and maintenance cost, have influence in the decision on the suitable treatment technique.

Passive treatments are based on naturally occurring biological, geochemical and physical processes. Wetlands and bioreactors are commonly used as biological processes, but problems like degradation of wetlands by AMD acidity (Prudêncio et al. 2015) and

the low flow rates of bioreactors can impair their use (Skousen et al. 2017). Geochemical passive treatments consist in the reaction of water with alkalinity-generating materials such as limestone and calcite-based permeable substrates (Ayora et al. 2016). Open limestone channels are often used, but the increasing pH leads to precipitation of metal hydroxides at the interface between the limestone gravel and AMD, known as armouring effect. These surface coatings impair limestone dissolution rate, decreasing the effectiveness of the treatment in 10-50% (Skousen et al. 2017).

Active processes are characterised by the continuous addition of chemicals to neutralise AMD. Lime is the most common material used to treat AMD, but anhydrous ammonia or sodium hydroxide can be used as well (Johnson and Hallberg 2005). In this case, there is no armouring effect, but co-precipitation of Fe/Al (hydr)oxides due to the pH increase helps to enhance removal of trace elements from wastewater. Some studies evaluated the use of Fe (hydr)oxides as surface sorption material for REE (Ghobadi et al. 2017; Unal Yesiller et al. 2013; Bagheriyan 2011). Such studies, however, just assessed adsorption or other surface sorption processes, but not co-precipitation.

The use of Fe (hydr)oxides for wastewater treatment is a good option because these compounds are common in nature and can be easily synthesised in laboratory (Schwertmann and Cornell 2003). A common method to synthesise isomorphically substituted Fe (hydr)oxides, particularly goethite and hematite, is to increase the pH of a mixed solution of iron salts and the substitute to precipitate ferrihydrite (co-precipitation route). However, the difference between the ionic radius of the involved elements must be evaluated. A difference up to about 15% allows the isomorphic substitution to occur at ambient temperatures for several ions. The most common ion that can replace up to 33% of Fe^{3+} atoms in goethite is Al^{3+}. As the Al^{3+} ion is smaller than Fe^{3+}, there is a decrease in the unit cell parameters of the crystals, leading to an increase in surface area, which also influences the adsorption capacity of Fe (hydr)oxides. It is unlike that REE isomorphically replace Fe^{3+}, given the difference between the ionic radii of these elements, but it could still be considered depending on the Fe (hydr)oxide structure. In fact, there are reports for isomorphic substitution of Fe or Fe-O groups by Ce on Fe (hydr)oxides (Mohapatra et al. 2005). Moreover, the possibility of adsorption and/or co-precipitation of these elements with Fe-oxides is a possibility that remains to be studied.

Co-precipitation of some trace elements such as Al, Cr, V, Mn, Mo, Co, Ni and Cu can modify the iron (hydr)oxides mineralogical phases, since they can isomorphically replace Fe (Schwertmann and Cornell 2003). This may even affect the stability of mineralogical phases in sludge from AMD treatment. The influence of structural Al in the stability of Fe (hydr)oxides is well known, but a little bit controversial when considered other elements associated to them. Schwertmann (1984) and Jeanroy et al. (1991), for example, attested a higher resistance to dissolution of hematite and goethite as the degree of Al isomorphic substitution increased. Silva et al. (2010) also reported an increase on stability of As associated to Al-goethites under reducing conditions. On the other hand, a decrease in stability of La and Ce co-precipitated with Fe (hydr)oxides was reported as the Al increased (Pietralonga et al. 2017; Barcelos 2014; Cardoso 2014). Therefore, the processes involved in this removal need to be more clearly understood, since the management of the resulting sludge depends on its chemical stability under local environmental conditions. The more stable is the material, the lower the risk of contamination due to its disposal. On the other hand, a less stable material may allow the recovery of economically interesting elements such as REE. Therefore, a sound understanding of this process is need to increase the efficiency and choose the best way to manage the sludge of wastewater treatment.

The use of Fe (hydr)oxides for wastewater treatment has been studied and several papers have already been published in the last decades. Contaminants considered in these studies included organochlorines (Varanasi et al. 2007; Wang and Zhang 1997), as well as trace elements such as uranium (Duff et al. 2002) and arsenic (Vasques et al. 2018; Mello et al. 2018; Abid et al. 2013; Mamindy-Pajany et al. 2011; Silva et al. 2010; Asta et al 2009; Cumbal and Sengupta 2005). On the other hand, similar studies with REE are still scarce and limited to adsorption processes (Ghobadi et al. 2017; Unal Yesiller et al. 2013; Bagheriyan 2011; Fendorf and Fendorf 1996).

Ghobadi et al. (2017) showed that magnetic nanoparticles of $Co_xMn_{1-x}Fe_2O_4$ (where x = 0.2 and 0.8) were efficient to adsorb La^{3+} and Ce^{3+} from water. Similar results were obtained by Unal Yesiller et al. (2013), who studied REE uptake by nano-zeo valent iron (nZVI) and alumina-supported nZVI. Bagheriyan et al. (2011), also successfully investigated the use of Fe(II) sulphide coated with nano magnetite for separation of La from aqueous solution. Finally, Fendorf and Fendorf (1996) obtained satisfactory results

for sorption of La in Mn, Fe and Ti (hydr)oxides by adding the contaminant over suspensions containing pre-formed (hydr)oxides. Therefore, as stated before, these authors did not deal with co-precipitation which is an important process in wastewater treatment.

Only recently co-precipitation processes have been considered. Li et al. (2016), for example, performed co-precipitation to concentrate REE from high salt groundwater previously to its detection by inductively coupled plasma mass spectrometry (ICP-MS). Other studies, such as Pietralonga et al. (2017), assessed the efficiency of Fe/Al (hydr)oxides co-precipitation to remove La from aqueous solution containing Fe, Al and La. These authors found high La removal efficiency from water at high pH, but the mechanisms and the influence of pH and Al content were not fully explored. The influence of pH and Al in La removal from water was further studied by Barcelos (2014), who also assessed the stability of the resulting precipitates. These authors achieved high removal efficiency of La from aqueous solutions, although results from Barcelos et al. (2018b) suggested some precipitation of La as segregated phases (lanthanite) from Fe/Al (hydr)oxides.

The removal of Ce from water by synthetic Fe/Al (hydr)oxides was also studied by Cardoso (2014). Results showed high removal of Ce from water by co-precipitation with Fe/Al (hydr)oxides, but the presence of Al tended to decrease the treatment efficiency. These results were related to the mineralogical phases in precipitates. Only magnetite was detected in the absence of Al and at low Ce concentrations, while goethite was also identified in the presence of Al or at high Ce concentrations. Water soluble phases were not detected, but the recovery of Ce from muds of the water treatment was high under reducing conditions. The presence of Al also decreased the Ce stability in precipitates.

It is noteworthy that water treatment by co-precipitation with Fe/Al (hydr)oxides can include at least three different processes: a) simultaneous precipitation of the contaminant with Fe/Al (hydr)oxides, but as segregated phases; b) occlusion of the contaminant in the structure of Fe/Al (hydr)oxides mineralogical phases; c) adsorption of the contaminant immediately after precipitation of Fe/Al (hydr)oxides. Such processes, however, are difficult to be identified by ordinary techniques like sequential extraction

procedures (SEP), X-ray diffraction (XRD) or scanning electron microscopy (SEM). SEP, for instance, does not allow to distinguish specific adsorption from occlusion or precipitation as segregated phases. Also, segregated nano-phases in small amounts are not easily detected by XRD or SEM. For this purpose, sophisticated techniques such as X-ray absorption spectroscopy (XAS) or high-resolution transmission electron microscopy (HRTEM) are need.

It is also important to consider the reversibility of adsorption processes. The low reversibility of adsorption involving oxyanions forming elements, such as phosphorus (P) and arsenic (As) is very well stablished. These elements are recognised to form strong complexes onto Fe/Al (hydr)oxides surfaces, so called specific adsorption. On the other hand, adsorption of alkaline metals by negative charged colloids, also known as non-specific process, is quite reversible. Transition metals, however, can be adsorbed onto both negatively charged colloids as well as positively charged Fe/Al (hydr)oxides, by specific and non-specific mechanisms. Among these elements are the majority of concerning contaminants, such as heavy metals and REE. Schwertmann and Cornell (2003) showed that cation adsorption reversibility onto Fe/Al (hydr)oxides depends on the strength of the metal-surface complex. For example, Pb is completely desorbed from goethite (Schwertmann and Cornell 2003), while Cu, Zn, Cd, Ni and Co are only partially desorbed (Brümmer et al. 1988). Similar studies for REE are still scarce. Therefore, assessing desorption/recovery of these elements co-precipitated with Fe/Al (hydr)oxides is warranted. The desorption of these elements may cause environmental pollution, but at the same time the REE recovery from water treatment muds may be economically and environmentally feasible.

The aims of the present study were:

1) To assess the efficiency of Fe/Al (hydr)oxides co-precipitation to remove Eu and Ho, from water in individual studies. In this case, the hypotheses tested were: a) that REE distribution in precipitates is a function of the Fe:Al molar ratio in the system; b) that REE individual behaviour can be different due to their different oxidation state and ionic radius; and c) that Eu and Ho may precipitate in segregated phases (as observed for La and Ce in previous studies).

2) To characterise the mineralogical phases in precipitates. In this case, the hypotheses tested were: a) that different Fe:Al:REE molar ratios may result in precipitation of different mineralogical phases; b) that the valence of iron may influence the mineralogical phases precipitated; and c) that co-precipitation at lower pH may favour poorly crystallised mineralogical phases.

3) To assess the efficiency of Fe/Al (hydr)oxides co-precipitation to treat wastewater contaminated by a mixed REE solution containing La, Ce, Eu and Ho. In this case, the hypotheses tested were: a) that distinct REE may behave differently due to their oxidation states and ionic radius; b) that the competition among REE from a mixed solution may affect the removal efficiencies due to differences in affinity between individual REE and the Fe/Al hydr(oxides); c) that the pH may affect REE removal from water; and d) that the REE behaviour may be partly controlled by the oxidation state of Fe in the system.

4) To test the stability of REE in precipitates face to BCR sequential extractions procedure. In this case, the hypotheses tested were: a) that the REE remain stable under natural environmental conditions after precipitation; b) that distinct REE co-precipitated with Fe/Al (hydr)oxides can be differently recovered by acidic, oxidative and reductive solutions; and c) that REE stability in precipitates depends on the mineralogical phases and the pH of the system.

The thesis comprises three chapters: The first one aimed to assess the efficiency of Fe/Al (hydr)oxides to treat water contaminated by Eu or Ho to understand the individual REE behaviour in the process. The second chapter evaluated the influence of La, Ce, Nd, Eu and Ho in the mineralogical phases co-precipitated with Fe/Al (hydr)oxides. In this case, Nd was considered because precipitates from previous studies on removal of La, Ce and Nd from water were also used. The third chapter aimed to assess the influence of Fe sources (ferrous and ferric), pH's (6.0 and 9.0) and Fe:Al molar ratio on the treatment of water contaminated with a mix of La, Ce, Eu and Ho by Fe/Al (hydr)oxides co-precipitation.

In addition to the efficiency of the water treatment, assessed in the first and third chapters, all three chapters dealt with characterisation of mineralogical phases as well as the stability of REE in the resulting precipitates.

2. Material and Methods

2.1. Experimental sets

The methodology applied in this study was developed over a series of treatments carried out using a range of experimental conditions to co-precipitate Fe/Al (hydr)oxides at different Fe:Al:REE molar ratios (Fig. 2). A completely randomized experimental design were considered with three replicates for each treatment.

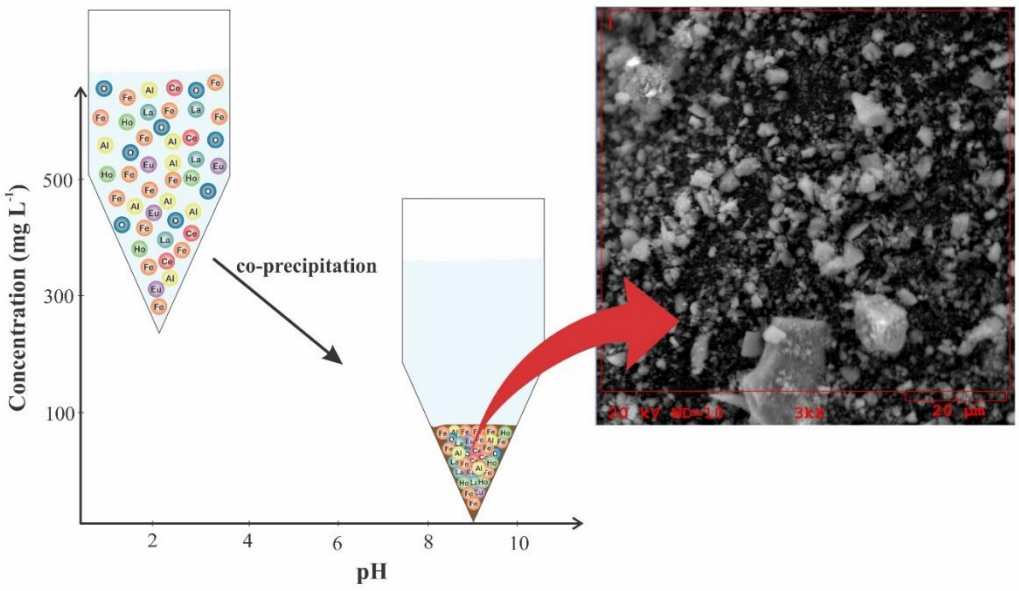

Fig. 2 Diagrammatic representation of experimental set

Fe/Al (hydr)oxides co-precipitation was performed based on Schwertmann and Cornell (2000) guidelines for syntheses of Al-substituted goethite and hematite. The main modifications were the use of sulphates instead of chlorides and pH values. Sulphates were used to simulate the typical conditions of water affected by acid mine drainage (AMD).

To test the hypothesis that the REE molar ratios affect their removal from water and the mineralogical phases co-precipitated with Fe/Al (hydr)oxides, different REE proportions were used in treatments. The absence of REE (blanks) was not considered in

any experimental set due to: a) previous studies revealed precipitation of magnetites and goethites from Fe(II) salts, respectively in the absence and presence of Al (Mello et al. 2018; Pietralonga et al. 2017; Barcelos 2014; Cardoso 2014) and hematite from Fe(III) salts (Schwertmann and Cornell 2000); b) inclusion of treatments with low concentrations of REE in relation to Fe and Al. Furthermore, blanks with REE, in the absence of Fe and Al were not included in treatments because it is well stablished the precipitation of REE oxides or carbonates in the pH range considered (Abrão 1994). This was also confirmed in previous tests performed in our laboratory.

Initially, two sets of experiments were conducted in order to evaluate the efficiency of iron and aluminium oxides in the removal of Eu and Ho, individually (Table 1). The solutions used were: 1 mol L^{-1} $FeSO_4.7H_2O$, 0.5 mol L^{-1} $Al_2(SO_4)_3.18H_2O$ and 10000 mg L^{-1} ICP standard solution, for Eu and Ho. The solutions were poured out into the flasks in the required quantities to obtain the molar ratios considered in the different treatments. Such molar ratios corresponded to concentrations of Eu and Ho in the range of highly contaminated wastewater, from 75.9 mg L^{-1} to 412.3 mg L^{-1}. The pH valued considered was 9.0, which is consistent with the maximum allowed for effluents discharge by Brazilian laws (CONAMA, 2011).

Table 1 Fe:Al:REE molar ratios for Eu and Ho treatments

Treatment with Eu	Fe: Al: Eu molar ratio	pH	Treatment with Ho	Fe: Al: Ho molar ratio	pH
Eu1	500 : 0 : 5	9.0	**Ho1**	500 : 0 : 5	9.0
Eu2	500 : 0 : 25	9.0	**Ho2**	500 : 0 : 25	9.0
Eu3	450 : 50 : 25	9.0	**Ho3**	450 : 50 : 25	9.0
Eu4	400 : 100 : 25	9.0	**Ho4**	400 : 100 : 25	9.0

In addition, two other sets of experiments were also conducted to evaluate the removal efficiency of a mixed REE solution. This was the first study that explores the efficiency of Fe/Al (hydr)oxides co-precipitation in order to treat a mixed REE solution. In these sets of experiments, the mixed solutions contained La, Ce, Eu and Ho.

Treatments were different Fe:Al:REE molar ratios combined with two Fe oxidation states (ferrous and ferric) and two pH values (Table 2). The sum of REE molar ratios made 50, being 12.5 for each one. Sulphates salts of iron (1 mol L^{-1} $Fe_2SO_4.7H_2O$ and 1 mol L^{-1} $Fe_2O_{12}S_3.8H_2O$), aluminium (0.5 mol L^{-1} and $Al_2(SO_4).18H_2O$), lanthanum (0.025 mol L^{-1} $La_2(SO_4)_3$) and cerium (0.1 mol L^{-1} $Ce(SO_4)_2$) were used. For Eu and Ho experiments, 10000 mg L^{-1} IPC standard solutions were used instead of sulphates. These solutions were poured out into the containers containing deionised water in the required amounts to obtain the considered Fe:Al:REE molar ratios (Table 2).

Table 2 Fe:Al:(La+Ce+Eu+Ho) molar ratios in the treatments

Treatment with Fe^{2+} salts	**Fe: Al: REE molar ratio**	**pH**	**Treatment with Fe^{3+} salts**	**Fe: Al: REE molar ratio**	**pH**
Fe(II)_1	500:0:50	9.0	**Fe(III)_1**	500:0:50	9.0
Fe(II)_2	400:100:50	9.0	**Fe(III)_2**	400:100:50	9.0
Fe(II)_3	100:400:50	9.0	**Fe(III)_3**	100:400:50	9.0
Fe(II)_4	500:0:50	6.0	**Fe(III)_4**	500:0:50	6.0
Fe(II)_5	400:100:50	6.0	**Fe(III)_5**	400:100:50	6.0

The use of Fe^{2+} and Fe^{3+} is due to the presence of both in AMD conditions, depending on the pH and oxidation rate of the ferrous ion. Besides, the REE removal from wastewater and stability of precipitates are expected to be influenced by the Fe valence. The use of Al aimed to evaluate its effects in the stability of co-precipitated phases (Barcelos et al. 2018a; Pietralonga et al. 2017; Silva et al. 2010; Jeanroy et al. 1991; Schwertmann 1984). Values considered for pH were 9.0 (six treatments) and 6.0 (four treatments), consistent with the range allowed for effluents discharge in Brazil (5.0 to 9.0) according to Resolution 430 of the Brazilian Environmental National Council (CONAMA, 2011).

To induce co-precipitation of the Fe/Al (hydr)oxides and REE, the pH was raised by adding 5 mol L^{-1} KOH. Twenty-four hours, 4 days and 7 days after the synthesis beginning, the pH was again adjusted with 5 mol L^{-1} KOH solution. Then, weekly the pH of the solution were measured and corrected using 5 mol L^{-1}, if necessary. Aliquots of

1mL of supernatant were collected before each measurement to monitor the concentration of the Eu and Ho remaining in solution as the experiment progresses.

To promote oxidation of Fe^{2+}, suspensions were submitted to air pumping into all containers for 1 hour daily, resuspending the material (Fig. 3). According to Schwertmann and Cornell (2000), daily swirling of the bottles is required to slow oxidise the suspensions. For 60 days, the experimental units were kept at room temperature (around 23ºC) and protected from direct sunlight. Thereafter, the supernatant was removed by siphoning and the precipitated material was recovered for analysis.

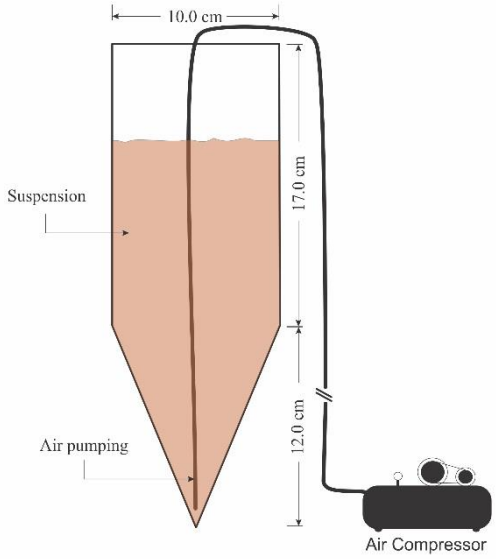

Fig. 3 Diagrammatic representation of containers and air pumping into the suspensions

In order to verify the efficiency of the treatments, Fe, Al and REE concentrations in the aliquots of supernatant collected were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). Then, concentrations were reported as a function of incubation time and the treatments efficiencies could be attested by comparing the initial and final REE concentrations in supernatants. Mass balance (MB) was also checked by comparing REE initial soluble concentrations (REE_{ISC}) with final soluble concentrations (REE_{FSC}) plus total contents in precipitates (REE_{TCP}) (Eq. 1). Quality

control for supernatants analyses included internal standards, check samples, spikes, standard synthetic solutions and replication.

$$MB = (REE_{ISC}) + (REE_{FSC}) + (REE_{TCP}) \quad \text{Eq. 1}$$

2.2. Characterisation of mineralogical phases in precipitates

At the end of the incubation period, the precipitates were collected, oven-dried, sieved (250 micron sieve) and prepared for analyses. Then, an aliquot of these materials was dialysed to remove the excess of soluble salts and the three replicates of each treatment were combined in a composed sample for mineralogical characterisation (XRD and SEM analyses). Another aliquot was used to assess the stability of REE in precipitates.

In order to assess the influence of REE in the mineralogical phases precipitated, X-ray diffraction analysis was performed to identify the solid phases in dialysed precipitates, using Co Kα ($\lambda = 0.1789$ nm), scanning angle range 2-70° and scan rate of 1 seg^{-1}. Diffractograms were interpreted based on data from Chen (1977), JCPDS (1974) and the American mineralogical society (Downs and Hall-Wallace 2003).

The samples were also examined by scanning electron microscopy (Leo SEM, model 1430VP) coupled to energy dispersive spectrometry (EDS). Micro chemical maps were obtained from selected areas and semi-quantitative EDS analyses were carried out on 5 spots per image. The surface area of precipitates was also assessed through BET isotherms with pure nitrogen as adsorbent. Samples were outgassed for 19h at room temperature as indicated by Clausen and Fabricius (2000).

Precipitates from previous studies with La (Barcelos 2014), Ce (Cardoso 2014) and Nd (unpublished data) were also included alongside with precipitates containing Eu and Ho in order to compare the influence of individual REE in Fe/Al (hydr)oxides precipitation (Table 3).

Table 3 Fe:Al:REE molar ratios in the treatments

Treatment	Fe:Al:REE molar ratio	pH	REE initial concentration (mmol L^{-1})
La1	500:0:5	11.7	0.50
La2	500:0:25	11.7	2.50
La3	500:0:50	11.7	5.00
La4	500:80:5	11.7	0.50
La5	500:160:5	11.7	0.50
Ce1	500:0:5	11.7	1.00
Ce2	500:0:50	11.7	10.00
Ce3	500:50:5	11.7	1.00
Ce4	500:100:5	11.7	1.00
Nd0	500:150:0	9.0	0.00
Nd1	500:150:0.5	9.0	0.97
Nd2	500:150:1	9.0	1.90
Nd3	150:350:0.5	9.0	0.97
Nd4	150:350:1	9.0	1.90
Eu1	500:0:5	9.0	0.50
Eu2	500:0:25	9.0	2.50
Eu3	450:50:25	9.0	2.50
Eu4	400:100:25	9.0	2.50
Ho1	500:0:5	9.0	0.50
Ho2	500:0:25	9.0	2.50
Ho3	450:50:25	9.0	2.50
Ho4	400:100:25	9.0	2.50

2.3. Stability and recovery of Eu and Ho from precipitated phases

To evaluate the potential of REE recovery from precipitates, all the 60 oven-dried samples were used without prior dialysis. The percentages of REE recovery were calculated from the total content measured by acid dissolution with *acqua regia* (3:1 HCl:HNO_3).

Water soluble phases were quantified by three sequential washes with deionised water, as suggested by Larios et al. (2012). An aliquot of 2 g from each one of all the 60 samples was used and submitted to 3 sequential washings using 40 mL, 40 mL and 20 mL of Milli-Q water, respectively. In each step the suspension was agitated in a horizontal shaker at 40 min^{-1} for 2 hours, followed by centrifugation at 4000 min^{-1} for 1 hour.

The resulting washed material was oven-dried and used for sequential extractions with the recommended BCR (Bureau Communautaire de Référence) solutions as suggested by Rauret et al. (1998). During the BCR sequential extractions, 0.5 g of sample was used in a ratio of 1:40 sample:extractor ratio. Acid soluble, reducible and oxidisable phases were extracted with 0.11 mol L^{-1} HCO_3H (acetic acid), 0.5 mol L^{-1} $NH_2OH \cdot HCl$ (hydroxylamine hydrochloride) and 8.8 mol L^{-1} H_2O_2 (hydrogen peroxide), respectively. BCR is among the simplest sequential extraction procedures that have been accepted as standard method for trace elements fractionation in soils and sediments (Mihajlovic et al. 2014; Rao et al. 2010; Pueyo et al. 2008; Wang et al. 2003; Ptistišek et al. 2001). Moreover, certified BCR-701 samples were added to the batches and submitted to the same procedure in order to ensure support in terms of method validation and quality control of the analyses.

The recovery percentage was calculated after determination of REE concentrations in each extraction step by inductively coupled plasma optical emission spectroscopy (ICP-OES). Results were compared by variance analysis and Tukey test at 5% significance level.

Publications and manuscripts submitted in this thesis

The content of one published paper and two submitted manuscripts is incorporated as part of the topics at section "3.0 Results and Discussion". The theoretical approach and project design were mainly conceived by the candidate with the support of the supervisors. The analysis and interpretation of the research data, as well as the writing process, were developed by the candidate with editorial support of the other authors and final critical review of the supervisor Jaime W. V. de Mello.

The topic 3.1 addresses the hypotheses relative to the aims 1 and 4 of the present study through the experiments of Eu and Ho removal from water by Fe/Al (hydr)oxides co-precipitation and assessment of the precipitates stability face to different extractors.

The topic 3.2 addresses the hypotheses relative to the study questions 2 and 4 though the analyses of samples from studies on Fe/Al (hydr)oxides co-precipitation to remove individual REE from wastewater, including samples of previous studies containing La, Ce and Nd.

The hypotheses from the studies questions 3 and 4 were addressed by the topic 3.3 through the evaluation of Fe/Al (hydr)oxides co-precipitation efficiency to treat wastewater contaminated by a mixed REE solution containing La, Ce, Eu and Ho.

3. Results and Discussion

3.1. Immobilization of Eu and Ho from aqueous solution by co-precipitation with Fe and Al (hydr)oxides

Concentrations of soluble Eu and Ho, as a function of time were below detection limit (DL_{Eu}=0.001 mg L^{-1} and DL_{Ho}=0.002 mg L^{-1}) during most of the incubation period, except for the fourth day after precipitation (Figs. 4 and 5). The peaks for Eu and Ho concentrations correspond to a decrease in pH (Fig. 6). On day 4th, the pH dropped to values below 6 which can be ascribed to oxidation of Fe^{2+} and consequent hydrolysis of Fe^{3+}, which releases H^+ ions according to the following equilibrium (Eq. 2).

$$4Fe^{3+}\ (aq) + 12H_2O\ (l) \leftrightarrow 4Fe(OH)_3\ (s) + 12H^+\ (aq) \qquad \text{Eq. 2}$$

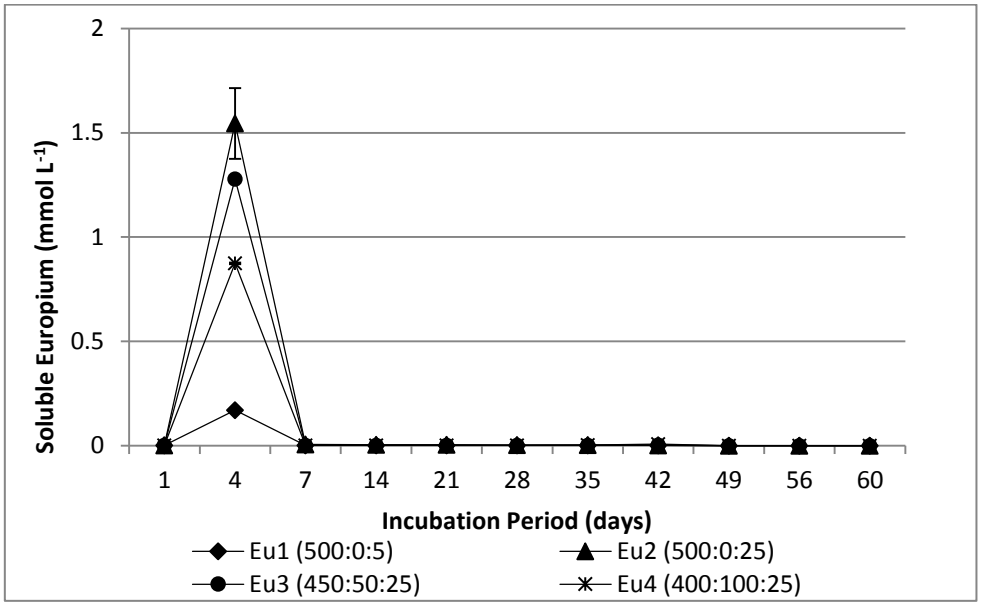

Fig. 4 Concentration of Europium in supernatants during the incubation period (mmol L^{-1})

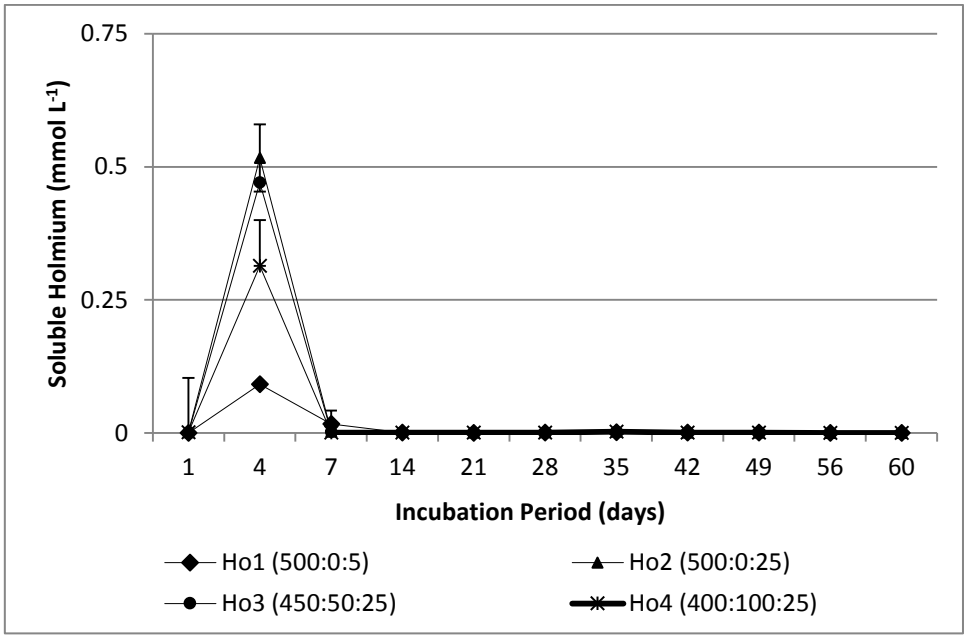

Fig. 5 Concentration of Holmium in supernatants during the incubation period (mmol L^{-1})

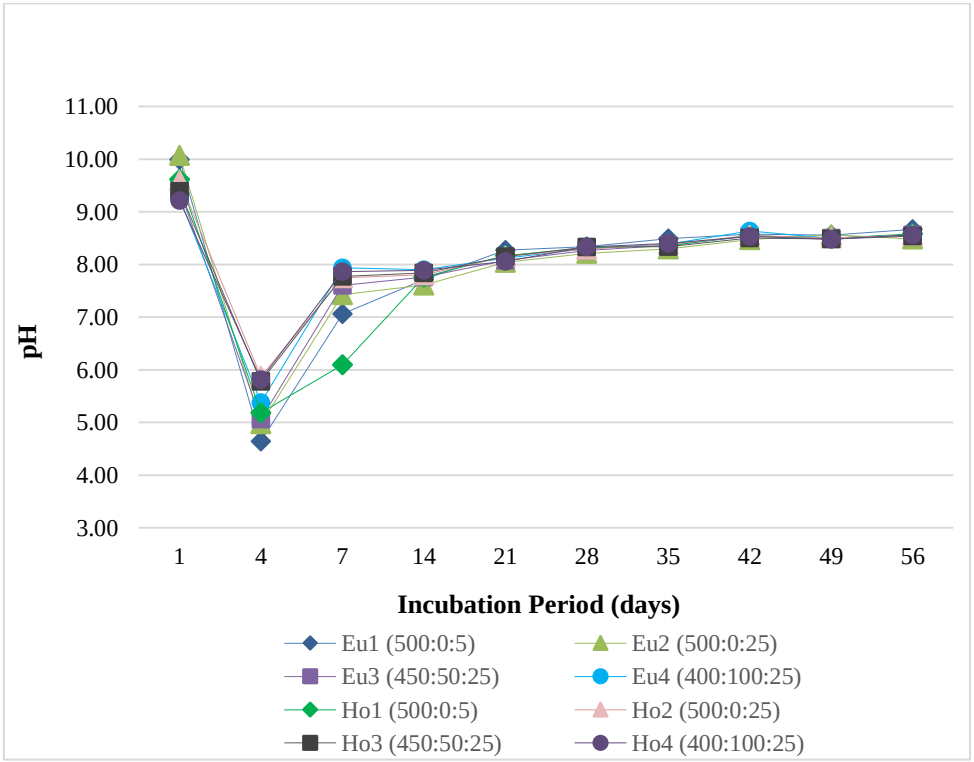

Fig. 6 pH measured during the incubation period of Eu and Ho treatments

After that decrease, pH was adjusted again by 5 mol L^{-1} KOH addition and values increased reaching a more stable condition in the range between 7.5 and 8.5 from 14 days until the end of incubation period. During this time the data suggest an almost complete removal of soluble Eu and Ho from water (Table 4).

It can be pointed out that contents of soluble Eu were higher than Ho in the peak of concentrations (day 4^{th}). Such observation does not agree with the expected solubilities of these elements, as Ho has been considered more soluble than Eu (Moldoveanu and Papangelakis 2012). Nevertheless, it can be also seen that pH decrease due to Fe (hydr)oxides precipitation was more accentuated in the presence of Eu than Ho. Then, it means that Eu favoured the precipitation of Fe, which could be ascribed to the reduction of Eu^{3+} to Eu^{2+} coupled to oxidation of Fe^{2+} to Fe^{3+} (Abrão 1994). Also, Eu^{3+} could precipitate as $Eu(OH)_3$ which is a very low solubility hydroxide (log K^o = -26.9 according to Spahiu and Bruno 1995). In this case, the increase of soluble Eu also should be ascribed to the dissolution of $Eu(OH)_3$ due to the decrease in pH (Eq. 3).

$$Eu(OH)_3\ (s) \leftrightarrow Eu^{3+} + 3OH^- \qquad \text{Eq. 3}$$

It can be considered that the release of H^+ ions due to the $Fe(OH)_3$ hydrolysis shifts the reaction (Eq. 2) towards the left, releasing Fe^{3+} ions, which explains the peak in Fe contents at the fourth day of incubation time (Fig. 7). It is also worth of note that the pH decrease in day 4^{th} is more expressive for Eu treatments leading to a higher increase also in Fe contents for these treatments when compared to Ho treatments at the same Fe:Al:REE molar ratio. When pH is adjusted back to 9.0 precipitation of $Fe(OH)_3$ takes place again, decreasing soluble Fe thereafter until the end of the incubation period

Table 4 Concentration of Eu and Ho in the end of the incubation period (60 days)

Treatment	Fe:Al:REE molar ratio	Concentration (mg L^{-1})
Eu1	500:00:05	0.002 ± 0.001
Eu2	500:00:25	0.011 ± 0.006
Eu3	450:50:25	0.010 ± 0.005
Eu4	400:100:25	0.005 ± 0.003
Ho1	500:00:05	0.002 ± 0.001
Ho2	500:00:25	0.007 ± 0.002
Ho3	450:50:25	0.008 ± 0.005
Ho4	400:100:25	0.006 ± 0.004

As expected, concentrations of Ho and Eu in the 4th day peak were higher as the initial concentrations of these REE increased. Notwithstanding, in treatments with maximum REE concentrations (i.e. Fe:Al:25 molar ratios), their soluble contents were lower as the Al increased. This means that Al stabilises the Fe (hydr)oxides which can be attested by the decrease of soluble Fe at the fourth day as Al contents increase in treatments with maximum REE concentrations (Fig. 7). It is well known that Fe (hydr)oxides containing structural Al, due to isomorphic substitution, are more resistant to reduction (Silva et al. 2010; Bousserrhine et al. 1999; Jeanroy et al. 1991; Torrent et al. 1987) and to the pH lowering (Schwertmann 1984).

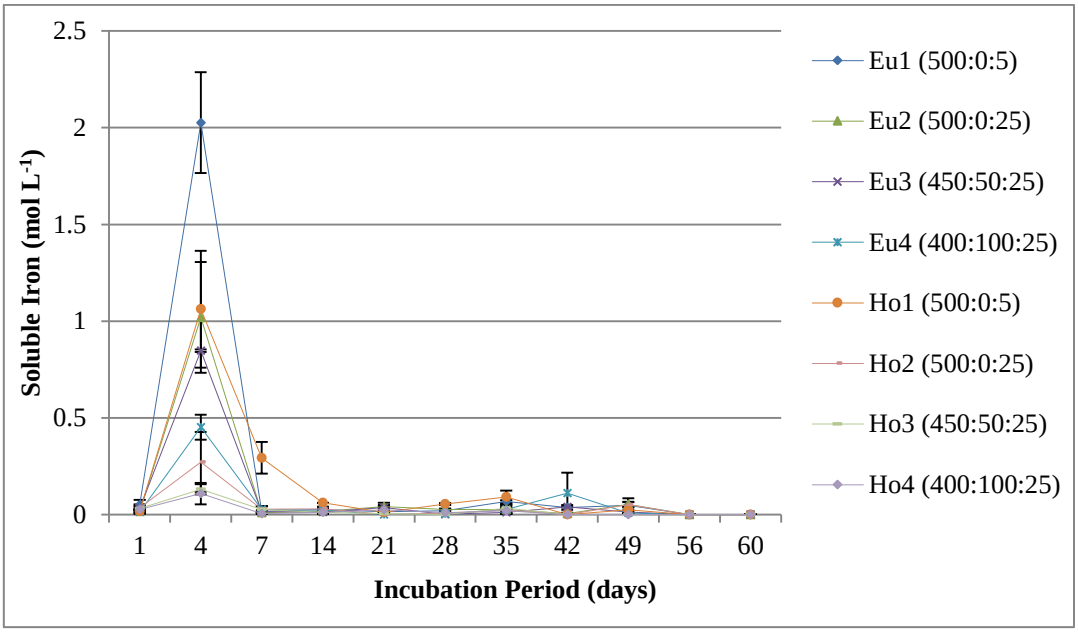

Fig. 7 Concentration of Iron in the supernatant during the incubation period (mg L^{-1})

In Brazil, the legal threshold for wastewater discharge is regulated by the resolution 430 of the National Environmental Council (CONAMA 2011). There are no requirements for wastewater containing REE in this document so far. In fact, the toxicological investigations on REE-associated health effects are scarce when compared to other contaminants. Hence, the level of adverse effects needs to be more understood before legal thresholds can be properly determined (Yang et al. 2016; Pagano et al. 2015a; Pagano et al. 2015b; Wey et al. 2013). Nonetheless, even considering the requirement for a highly toxic element such as Arsenic (0.5 mg L^{-1}), it is feasible to suppose that the final concentrations of Eu and Ho would fulfil the legislation for safe discharge of the treated water. The higher concentrations at the end of the incubation period were around 0.01 mg L^{-1} (Table 4), which is about 50 times less than the requirements for Arsenic, an admittedly harmful element (Gupta and Chatterjee 2017; Ravenscroft et al. 2009).

Removal efficiencies were calculated based on Eu and Ho concentrations at the beginning and at the end of incubation period (Table 5). All treatments showed high removal efficiencies, with no significant differences among them. Such results, are in line with previous studies (Pietralonga et al. 2017; Barcelos 2014; Cardoso 2014) showing that precipitation of Fe/Al (hydr)oxides is effective to treat wastewater containing REE. Therefore, the presence of Al as well as Eu and Ho initial concentrations did not interfere

in the removal process of these REE from water. Notwithstanding, such variables could affect the stability of the precipitates, as discussed later.

It is worth of note that the high efficiencies of the treatments were comparable to previous studies irrespective to incubation period and pH. Pietralonga et al. (2017) for example, incubated their treatments of La contaminated water for 90 days, compared to a 60-day period in this study for Eu and Ho. It is also relevant to compare the adopted pH's for precipitations. In that previous studies, it was considered the pH 11.7 as recommended by Schwertmann and Cornell (2000) to synthesise aluminium substituted goethites. In the present study, pH 9.0 was adopted due to Brazilian legal regulations for discharge of wastewater. This represents an important economy in terms of mining wastewater management.

Table 5 Eu and Ho Removal efficiency (%)

Treatment	**Fe:Al:REE molar ratio**	**REE initial concentration (mmol L^{-1})**	**Removal Efficiency**	
			Eu	**Ho**
Eu1	500:00:05	0.50	100.00	
Eu2	500:00:25	2.50	100.00	
Eu3	450:50:25	2.50	100.00	
Eu4	400:100:25	2.50	100.00	
Ho1	500:00:05	0.50		100.00
Ho2	500:00:25	2.50		100.00
Ho3	450:50:25	2.50		100.00
Ho4	400:100:25	2.50		100.00

3.1.1. Stability and recovery of Eu and Ho from precipitated phases (BCR sequential extractions)

Water Soluble phases

Concentrations of soluble REE obtained by leaching with Milli-Q water (three sequential washings) were below the detection limits, excepted for Eu in treatment with 400:100:25 Fe:Al:Eu molar ratios. This represented less than 0.01% respective to the total amounts measured by *acqua regia* acid digestion (Table 6). These results attest the stability of Eu and Ho in the mud resulting from all treatments regarding water leaching. Similar results were obtained by Cardoso (2014) and Barcelos (2014), who treated water contaminated with Ce and La, respectively, by precipitation of Fe/Al (hydr)oxides.

Table 6 REE recovery (%) after the 3 sequential washings

Treatment	Fe:Al:REE molar ratio	Total contents (mg/kg)		Recovery (%)	
		Eu	Ho	Eu	Ho
Eu1	500:00:05	6049.96		<DL	
Eu2	500:00:25	29661.80		<DL	
Eu3	450:50:25	31270.33		<DL	
Eu4	400:100:25	30831.07		0.0055	
Ho1	500:00:05		7226.86		<DL
Ho2	500:00:25		25168.55		<DL
Ho3	450:50:25		26479.51		<DL
Ho4	400:100:25		29668.21		<DL

DL_{Eu} = 0.003 mg L^{-1}; DL_{Eu} = 0.012 mg L^{-1}

Acid leaching, reducible and oxidisable phases

The sum of Eu and Ho amounts recovered by the BCR sequential extractions steps was related to the initial contents of these REE in the treatments (Figs. 8 and 9). The higher were the initial contents the higher were the percentages recovered respective to *acqua regia* total amounts (Table 6). This means that the crystal phases stability is impaired by increasing content of REE associated to precipitates. There were no significant differences among treatments with the higher initial concentration of REE, irrespective to the Fe:Al molar ratio ($p<0.05$). This indicates that the presence of Al does not affect the stability of Eu and Ho in the precipitates.

Results for individual BCR sequential analyses showed that the acid leaching step (Acetic Acid 0.11 mol L^{-1}) was the one which extracted higher amounts for both Eu and Ho. Rare earth elements extracted by acetic acid are in general addressed to exchangeable and carbonate phases (Mittermüller et al. 2016; Schintu et al. 2016; Okoro et al. 2012). In the present case, carbonates were not detected by XRD (Figs. 13 and 14). These results, however, do not exclude the occurrence of carbonates, but mean they just can be present as minor phases, if so.

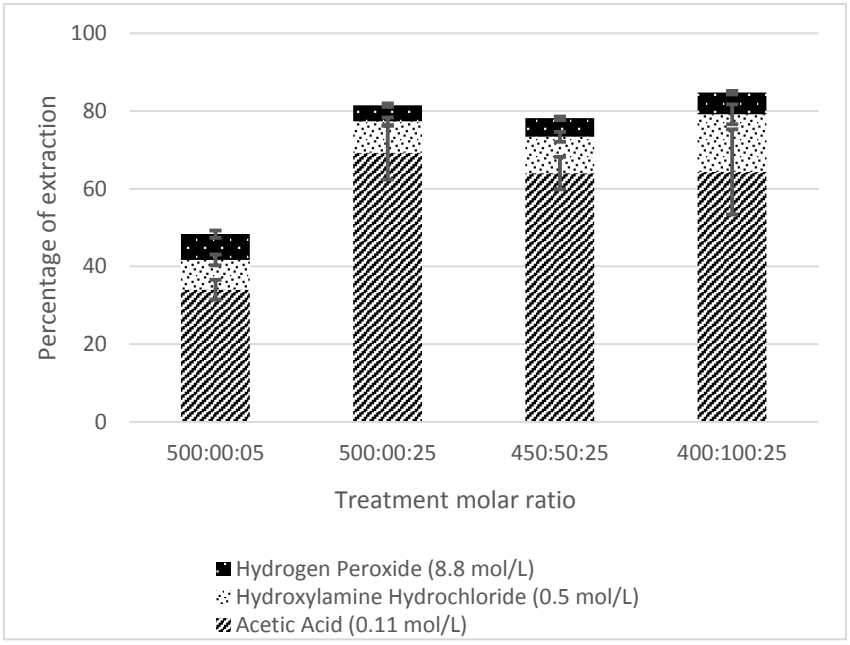

Fig. 8 Percentage of Eu recovered from precipitates by the three-step sequential extractions

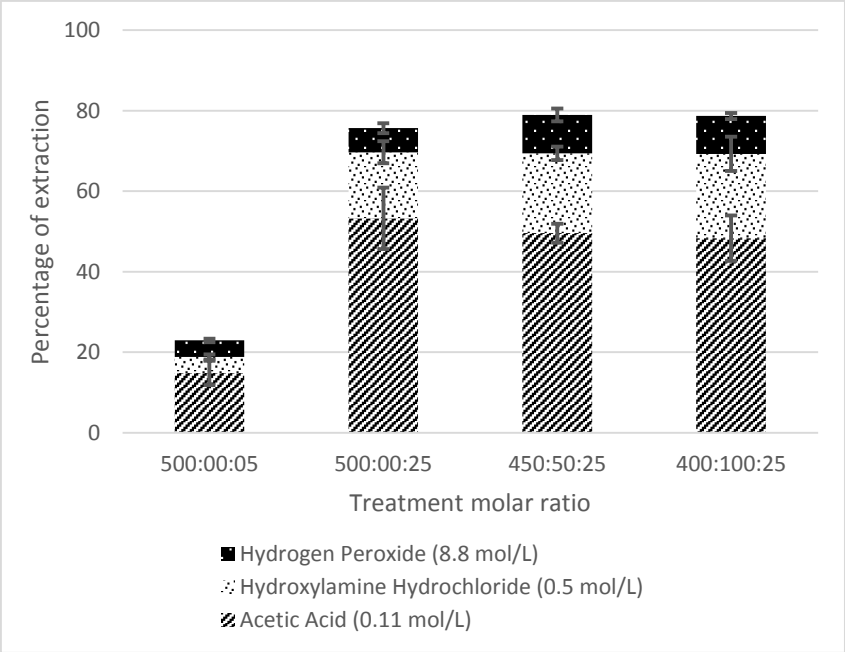

Fig. 9 Percentage of Ho recovered from precipitates by the three-step sequential extractions

Recovery by acetic acid extraction decreased as increased the Fe:REE molar ratios, in the absence of Al (Figs. 5 and 6). It means that increasing concentrations of REE restrains the stability of the sludge from water treatment, probably due to lower crystallinity of Fe (hydr)oxides. This is also suggested by narrowing and increasing intensity of XRD peaks as REE concentrations decrease (Figs. 13 and 14). Higher stability of REE in the sludge can also be ascribed to the presence of well crystallized magnetite as suggested in previous studies with La (Barcelos 2014) and Ce (Cardoso 2014).

Previous studies with REE showed that magnetite precipitates in the absence of Al and goethite is favoured by Al presence (Figs. 13 and 14). Precipitation of magnetite in the absence of Al was confirmed in the present study, but the peaks intensities decrease as the REE increase and, apparently goethite was not favoured by the presence of Al. Bands corresponding to poorly crystalized lepidocrocite were detected at higher amount of Eu, but the intensities decreased as Al increases. Such results agree with the study of Pietralonga et al. (2017) that showed the increasing in lanthanum contents favour the precipitation of lepidocrocite, in addition to lanthanite. Goethite peaks are more prominent in the absence of Al at low amounts of Eu, which is not evident for Ho, but the intensities for magnetite peaks were higher in the presence of Ho than in the presence of

Eu. This is another evidence that magnetite is the mineral responsible for higher stability of REE in precipitates as the contents of Eu extracted by acetic acid are, in general, higher than Ho.

Since the extraction with Acetic Acid was addressed to exchangeable phases, presumably adsorbed onto Al/Fe (hydr)oxides, it can be expected that the surface area influences the extractable amounts. As the isomorphic substitution of Fe by Al on goethite is recognized to increase the specific surface (Schulze 1984), it is reasonable to suppose that the presence of goethite is responsible for a higher adsorption of REE while they are rather co-precipitated with magnetite. Zhang et al. (2003) suggested the Ce could fit between the magnetite crystal plans. If Ce which has an ionic radius of 1.034 Å is able to fit inside magnetite's crystal structure, it is plausible suggest that Ho (0.901 Å) and Eu (0.947 Å) could fit as well. This way, the amount and crystallinity of magnetite seems to be important to define the stability and recovery of REE from the sludge of water treatment.

Second (Hydroxylamine Hydrochloride 0.5 mol L^{-1}) and third (Hydrogen Peroxide 8.8 mol L^{-1}) steps of BCR method, in general, extracted lower amounts of Eu than Ho (Figs. 8 and 9). This is mainly due to reducible phases, as hydroxylamine was able to recover higher amounts of REE than hydrogen peroxide (oxidisable phases). Nevertheless, these results are not in line with findings from Rao et al. (2010), who obtained higher amounts of reducible phases compared to the acid extractable ones. In fact, Rao at al. (2010) found that the amounts recovered by hydroxylamine was even superior to pseudo-total contents extracted by *acqua regia*. The authors suggest the REE were trapped into refractory oxides along with Fe and Mn oxides structures that could not be fully attacked by *acqua regia*. In the present study, however, the total contents extracted by *acqua regia* were much higher than the BCR extractable phases, and compatible with theoretical values calculated based on the reagent concentrations used for the synthesis.

It is well known that hydroxylamine extracts the elements associated to Fe (hydr)oxides by reductive dissolution (Aomi et al. 2013; Whalley and Grant 1993). Therefore, our results suggest that at least part of Ho is inside the Fe (hydr)oxides structures, as its contents extractable by hydroxylamine were higher while the contents

extractable by acetic acid were lower compared to Eu. On the other hand, Eu is probably rather associated to adsorbed phases onto minerals surfaces extractable by acetic acid. The remaining REE contents, that were not recovered by BCR sequential extractions, are probably associated to phases that could not be extracted by reductive dissolution, maybe refractory oxides as suggested by Rao el al. (2010).

Hydrogen Peroxide extraction refers to oxidisable fractions which were low compared to other BCR fractions. In fact, oxidisable phases were not found in the precipitates excepted magnetite. However, the results obtained by hydrogen peroxide does not allow to assure extraction of REE from magnetite oxidation.

3.2. Characterisation and stability of Fe/Al (hydr)oxides mineralogical phases synthesised in the presence of La, Ce, Nd, Eu and Ho

3.2.1. Mineralogical Characterization of Precipitated Phases

As stated before, precipitates from previous studies with La (Barcelos 2014), Ce (Cardoso 2014) and Nd (unpublished data) were analysed alongside with Eu and Ho precipitates in order to compare the influence of individual REE in Fe/Al (hydr)oxides precipitation (Table 3).

Varying in Fe:Al:REE molar ratios provided precipitation of different (hydr)oxides mineralogical phases. In addition, pH, redox potential and aeration can drive synthesis of selected phases (Schwertmann and Taylor 1989).

In general, for La treatments higher amounts of Al favoured precipitation of goethite (FeOOH) rather than magnetite (Fe_3O_4), as also observed by Silva et al. (2010). Magnetic activity was detected at high Fe:Al molar ratios or at the absence of Al in precipitates containing La (Fig. 10). On the other hand, isomorphic substitution of Fe by Al drives precipitation of goethite (Gt), since this mineral is able to incorporate more structural Al than magnetite (Schwertmann and Murad 1990). Increasing amounts of Al also favoured precipitation of gibbsite ($Al(OH)_3$) and lepidocrocite (FeOOH), as also observed by Pietralonga et al. (2017).

The presence of La also seems to impair magnetite synthesis. Besides the XRD detection (Fig. 10), magnetic activity and dark coloration in precipitates were further observed in treatments with lower amounts of La (high (Fe+Al):La molar ratios). Increasing amounts of La favoured precipitation of goethite (Gt) and lepidocrocite (Lp) as also noticed by Pietralonga et al. (2017). In addition to these minerals, lanthanite ($La_2(CO_3)_3.8(H_2O)$) was also detected in treatments La2 (500:0:25 Fe:Al:La) and La3 (500:0:50 Fe:Al:La), confirming the segregation of this REE at lower (Fe+Al):La molar ratios, even at lower La amounts than observed by Pietralonga et al. (2017). These results indicates that the excess of La in solution at higher pH promote the capture of CO_2 from the atmosphere, precipitating as carbonates.

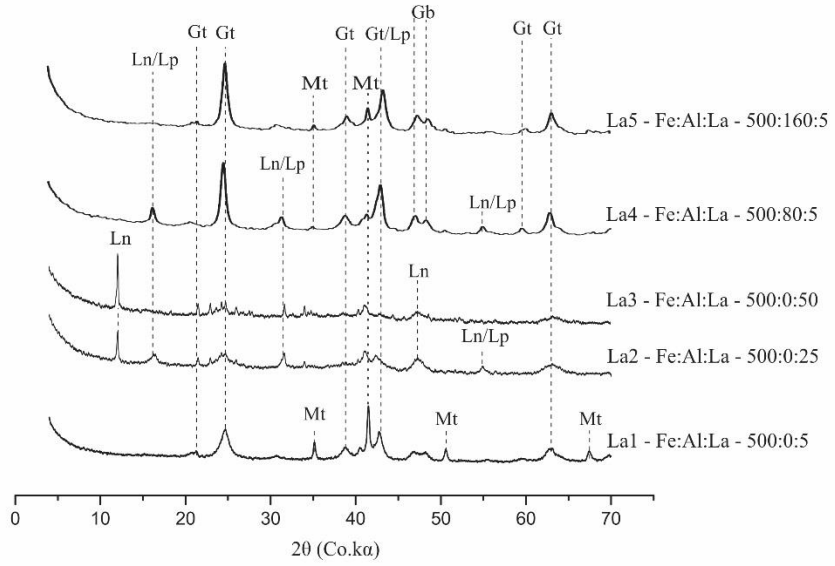

Fig. 10 XRD patterns of precipitates containing Lanthanum. Gt – Goethite; Gb – Gibbsite; Mt – Magnetite; Ln – Lanthanite; Lp – Lepidocrocite.

Magnetite was also detected in precipitates from Ce experiments, but unlike La precipitates, such mineral was detected in all treatments with Ce, irrespective to the Fe:Al:Ce molar ratio (Fig. 11). At the lowest amount of Ce and in the absence of Al (500:0:5 Fe:Al:Ce), only magnetite was detected, but XRD features of this mineral changed as Ce amounts increased. Magnetite peaks were broadened, indicating lower crystallinity degree and goethite was further detected as (Fe+Al):Ce molar ratios decreased. These effects can be ascribed to electron transfer from Fe^{2+} coupled to Ce^{4+} reduction, promoting oxidation of magnetite to goethite. Zhang et al. (2003) observed

similar results, suggesting collapse of the crystalline structure in Ce doped magnetite. On the other hand, such effects were not observed in Ce doped goethite. Mohapatra et al. (2005) also reported higher capability of goethite to incorporate Ce without significant changes in its structures. This is probably the reason why the increase in Ce concentration did not lead to precipitation of lepidocrocite, differently of other REE in this study.

Cerianite (CeO_2) was detected by XRD indicating segregation of Ce from iron (hydr)oxides. This was observed in precipitates of the experiment with Cerium at a 500:0:50 - Fe:Al:Ce molar ratio (Fig. 11). Mohapatra et al. (2005) also detected CeO_2 at Fe:Ce molar ratios lower than 29:1. According to the authors, it initially precipitated as amorphous $Ce(OH)_4$ from aqueous solution containing both Fe and Ce and then crystallised as CeO_2.

Goethite formation was expected in treatments containing Al as it presents a greater capacity of Al uptake in the structure compared to magnetite (Schwertmann and Murad 1990). Nevertheless, Gt was only detected by XRD as a minor phase in Ce experiments, with increasing expression at higher amounts of Ce and Al (Fig. 11). It seems that the amounts of Al used in this study were not enough to promote an expressive formation of goethite in the presence of Ce. On the other hand, Ce seems to have favoured goethite formation at lower concentrations than Al did. Ce might have hindered Fe^{2+} entry in the magnetite structure by enhancing Fe^{2+} oxidation rate. Since the standard redox potential for Ce^{4+}/Ce^{3+} (1.61 V) is higher than for Fe^{3+}/Fe^{2+} (0.77 V), the oxidation of Fe^{2+} coupled to reduction of Ce^{4+} is a plausible hypothesis.

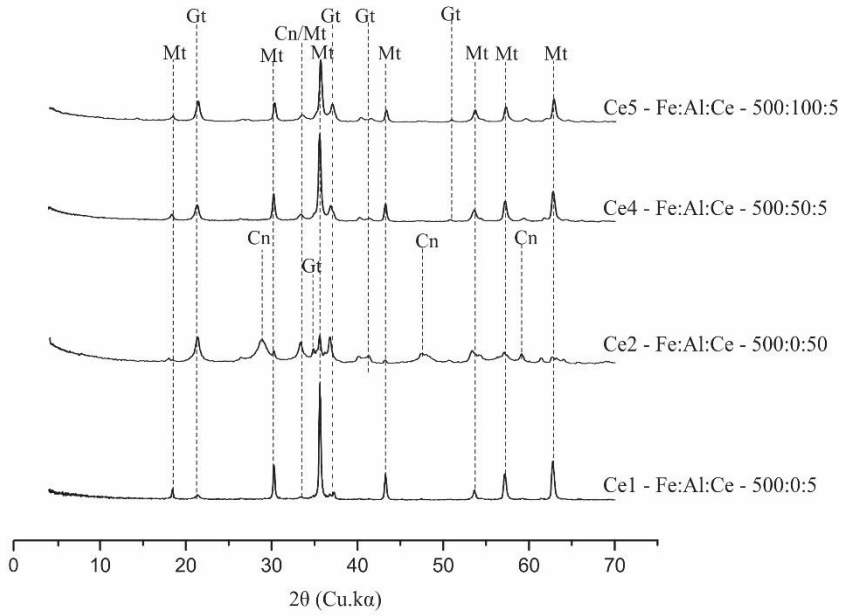

Fig. 11 XRD patterns of precipitates containing Cerium. Cn – Cerianite; Gt – Goethite; Mt – Magnetite.

Goethite (Gt) and gibbsite (Gb) were the predominant mineralogical phases in experiments containing Neodymium (Fig. 12). For treatments with 500:150 Fe:Al molar ratio, the presence of Nd favoured precipitation of lepidocrocite in addition to goethite. The presence of lepidocrocite is usually associated to a decrease in REE stability in the precipitates as observed for Eu (Barcelos et al. 2018), La (Pietralonga et al. 2017) and Ce (Cardoso 2014). Precipitation of gibbsite was favoured at 150:350 Fe:Al molar ratio due to oversaturation relative to structural Al in Fe (hydr)oxides (Schwertmann and Cornell 2003). Unlike the other REE studies, magnetite was not detected in the presence of Nd, but this can be ascribed to the higher concentrations of Al used in this experiment relative to the other ones. Anyhow, Nd seems to impair precipitation of magnetite because it was slightly detected in the absence of Nd.

Unlike what happened in La and Ce studies, Nd segregated phases were not detected by XRD in precipitates. It could be hypothesised that Nd might fit in the structure of Fe (hydr)oxides due to its smaller atomic radius (0.983Å) relative to La (1.032 Å) and Ce (1.01 Å) (Shannon 1976).

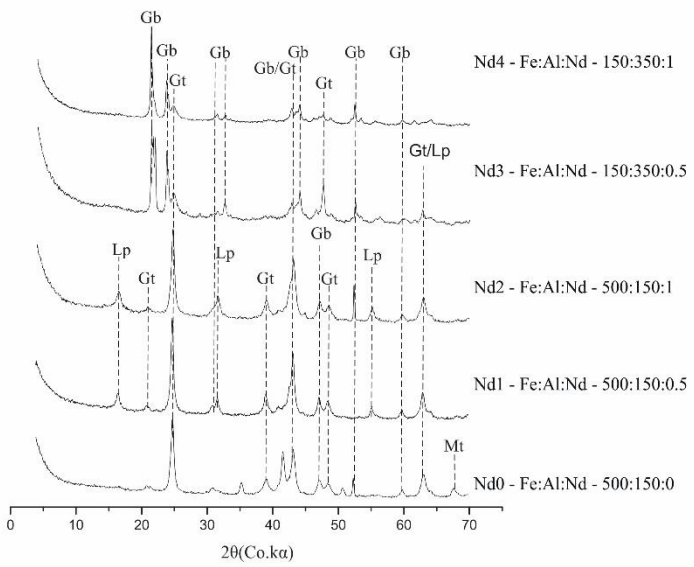

Fig. 12 XRD patterns of precipitates containing Neodymium. Gb – Gibbsite; Gt – Goethite; Lp – Lepidocrocite; Mt – Magnetite.

A narrowing and increasing intensity of XRD peaks was noticed as Eu and Ho concentrations decreased (Figs. 13 and 14). As observed for other REE, magnetite precipitation was favoured in the absence of Al and goethite was favoured by its presence. However, increase in REE contents led to a decrease in intensities of magnetite peaks. Apparently, presence of Al did not favour precipitation of goethite in detriment to magnetite as for the other REE. Even at lower Fe:Al molar ratios, precipitation of magnetite was observed. Higher Eu contents led to precipitation of poorly crystalized lepidocrocite, but the intensities decreased as Al contents increased (Fig. 13).

In the absence of Al goethite peaks were more prominent at low than at high amounts of Eu (Fig. 13), which was not observed for Ho (Fig. 14). On the other hand, intensities of magnetite peaks were higher for Ho than for Eu treatments. Even at high Ho contents, magnetite was the dominant phase respective to goethite. Such results were confirmed by the dark colour and magnetic activity observed for Ho treatments. In addition, the predominance of magnetite led to a higher stability of Ho in precipitates face to acid leaching, as will be discussed later. These results could be ascribed to the smaller ionic radius of Ho which probably would allow it to develop a stronger association with magnetite in relation to Eu. This stability can also be endorsed by a better crystallisation, noticed by narrowed peaks of magnetite in Ho than in Eu treatments.

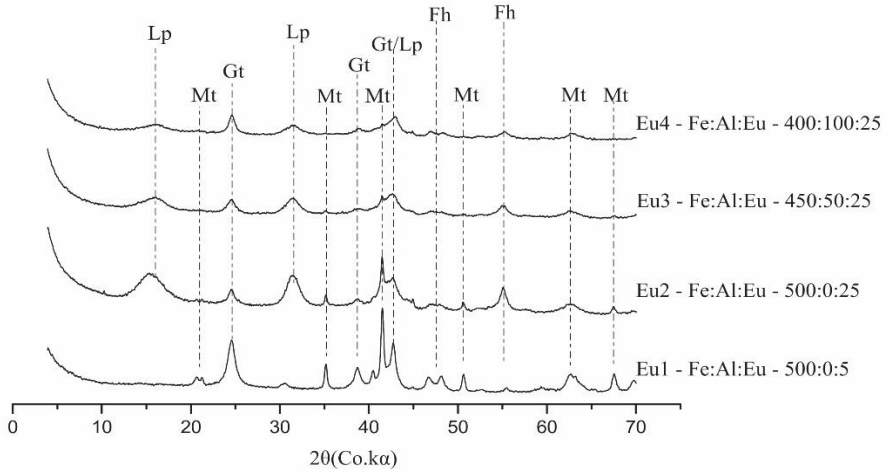

Fig. 13 XRD patterns of precipitates containing Europium. Fh – Ferrihydrite; Gt – Goethite; Lp – Lepidocrocite; Mt – Magnetite.

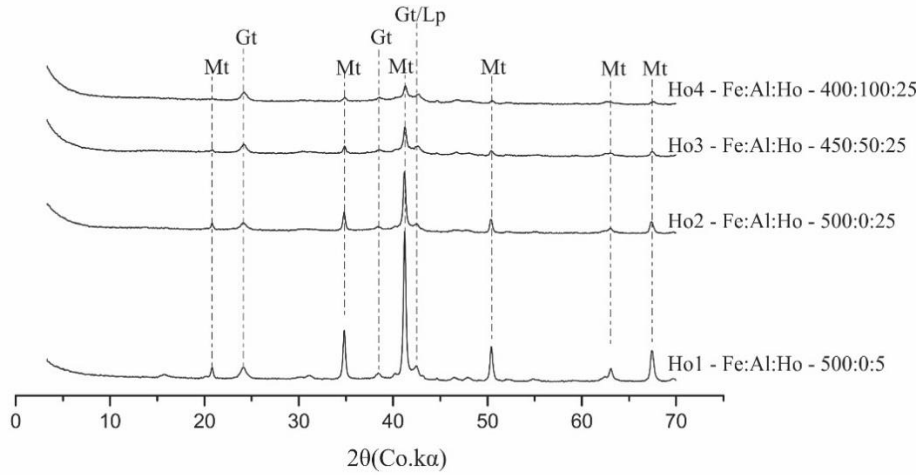

Fig. 14 XRD patterns of precipitates containing Holmium. Gt – Goethite; Lp – Lepidocrocite; Mt – Magnetite.

Some mineralogical features, as detected by XRD, could also be attested by scanning electron microscopy (SEM) images and elemental composition at selected spots of the samples. SEM images can also help to better understand the precipitates stability as it depends on the composition, chemical structure and surface morphology of mineral phases (Fendorf and Fendorf 1996). In general, elemental distribution in the samples appeared uniform in the microchemical maps, irrespective to Fe:Al:REE molar ratios, excepted La. A different pattern emerged in treatments at high La concentrations. Under such conditions, segregation of La was detected, which is in accordance with Hayes and

Leckie (1986) who observed La agglomerates at the surfaces of Fe oxides at high La concentrations. According to these authors, a layer of La onto goethite surface is favoured in detriment of its incorporation in the mineral structure. Pietralonga et al. (2017) also observed La segregation for treatments with (Fe+Al):La molar ratio of 6:1. In our study, the presence of lanthanite was observed by XRD, at 500:0:25 and 500:0:50 Fe:Al:La molar ratios, indicating that segregation takes place at a lower concentration of La, namely 20:1 (Fe+Al):La molar ratio (La2 treatment). However, in SEM analysis segregation was confirmed only at high La concentration (Fig. 15 and 16), in treatment La3 (500:0:50 Fe:Al:La molar ratios).

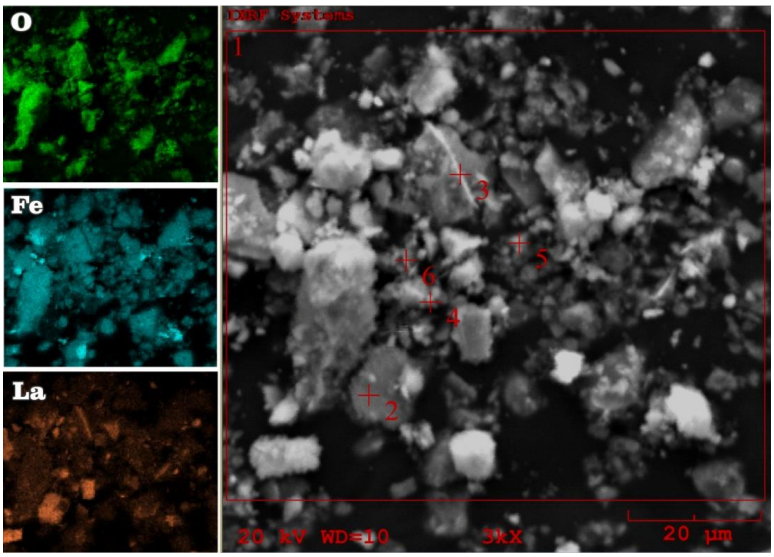

Fig. 15 SEM images of minerals synthesised from treatment La3 (Fe:Al:La - 500:0:50) with microchemical maps and backscattered electron image

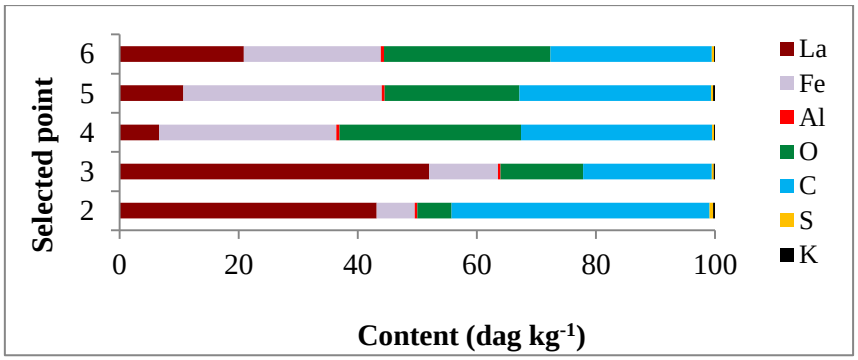

Fig. 16 Chemical composition of selected spots from treatment La3 (Fe:Al:La - 500:0:50) obtained by energy dispersive spectrometry (EDS) analysis

On the other hand, segregation of other REE was not detected through SEM images, even though the presence of cerianite had been observed by XRD. Segregation of Ce was not detected by Mohapatra et al. (2005) in TEM images either, although XRD patterns of the heated samples (373K) suggested segregations of Ce (hydr)oxides nanoparticles. These results might be due to SEM technical limitations to detect nanoparticles segregated phases.

As discussed before, perhaps the smaller ionic radii of Nd, Eu and Ho compared to La and Ce allow a stronger association of those elements with Fe/Al (hydr)oxides. This could explain why segregated phases of such elements were not detected neither by XRD nor by SEM analyses. Even though La and Ce treatments were performed at a higher pH than Nd, Eu and Ho treatments, previous studies also reported the presence of La segregation as lanthanite for treatments at pH 7.5 (Barcelos 2014). Therefore, the difference in pH among treatments considered in the present study should not affect this observation.

3.2.2. REE stability on Precipitates

Regardless the mineralogical phases detected and the REE involved, in general, precipitates of all treatments were stable face to the sequential washings (Table 7). The recoveries of Ce and Ho were quite low for all treatments, as well as most of Eu treatments as their soluble contents were lower than the detection limits. For La, the water soluble contents were less than 0.1 mg kg^{-1}, i.e. percentage recoveries lower than 0.001%. Neodymium presented the highest recovery percentages, but still below 0.02% or less than 6.0 mg kg^{-1}.

Unlike other REE, significant differences in Nd stability were detected by water extractions, which can be ascribed to the mineralogical phases found in the precipitates. Treatments with predominance of gibbsite (Nd3 and Nd4) presented higher concentrations of soluble Nd and treatments with predominance of goethite (Nd1 and Nd2) were more stable. In general, higher Nd recoveries respective to other REE can also be related to the absence of magnetite. The presence of this mineral has been associated

to an increase in stability of Eu, Ho (Barcelos et al. 2018) and La (Pietralonga et al. 2017) co-precipitated with Fe/Al (hydr)oxides. The major presence of magnetite and goethite seemed to stabilise the other REE in precipitates. Even treatments with the presence of segregated La and Ce phases (La2, La3 and Ce2, respectively) were stable face to water extractions.

Table 7 Soluble contents and recovery of REE from precipitates by water

Treatment	Fe:Al:REE Molar ratio	Total content (mg kg^{-1})	Water soluble phase (mg kg^{-1})	Recovery Percentage (%)
La1	500:00:05	11538.41	0.01 ± 0.03	0
La2	500:00:25	57159.91	0.13 ± 0.04	0
La3	500:00:50	98964.50	0.13 ± 0.01	0
La4	500:80:5	9049.17	0.08 ± 0.02	0
La5	500:160:5	8175.71	0.08 ± 0.03	0
Ce1	500:00:05	6490.29	<DL	<DL
Ce2	500:00:50	94436.36	<DL	<DL
Ce3	500:50:05	13585.95	<DL	<DL
Ce4	500:100:5	11992.19	<DL	<DL
Nd1	500:150:0.5	9814.24	1.33 ± 0.02	0.01
Nd2	500:150:1	19850.75	1.81 ± 0.01	0.01
Nd3	150:350:0.5	13723.95	2.69 ± 0.01	0.02
Nd4	150:350:1	28065.29	5.59 ± 0.02	0.02
Eu1	500:00:05	5662.19	<DL	<DL
Eu2	500:00:25	25365.39	<DL	<DL
Eu3	450:50:25	27647.40	<DL	<DL
Eu4	400:100:25	27249.24	0.01 ± 0.01	0.01
Ho1	500:00:05	6855.23	<DL	<DL
Ho2	500:00:25	25617.82	<DL	<DL
Ho3	450:50:25	25040.06	<DL	<DL
Ho4	400:100:25	28116.62	<DL	<DL

DL_{La}= 0.003 mg L^{-1}; DL_{Ce}= 0.05 mg L^{-1}; DL_{Nd}= 0.003 mg L^{-1}; DL_{Eu}=0.0031 mg L^{-1};DL_{Ho}= 0.0043 mg L^{-1}

Acid soluble phases were also assessed after water leaching of precipitates. In general, recovery by acetic acid decreased as increased the Fe:REE molar ratios, in the absence of Al (Fig. 17). Then, increasing concentrations of REE impairs their stability in the precipitates from water treatment, probably due to effects on crystallinity of Fe (hydr)oxides as discussed before. Higher REE stability in precipitates can also be related to the presence of magnetite as suggested in previous studies with Eu, Ho (Barcelos et al. 2018), La (Pietralonga et al. 2017) and Ce (Cardoso 2014). In general, intensity of magnetite peaks decreases, and other minerals precipitate instead, as REE contents increase in precipitates from water treatments. It can also be seen that recovery rates for La, Nd and Eu are higher than for Ce and Ho (Fig. 17), which presented predominance of magnetite respective to other mineralogical phases. These results again evidence the role of magnetite on the REE stability in precipitates and not just of pH. Even though La treatments were performed at higher pH (11.7) than Nd, Eu and Ho treatments (9.0) La was less stable than Ho. Notwithstanding, recovery rates were higher for Ho than for Ce, even when the Fe:Ho was twice the Fe:Ce molar ratio. This suggests further factors influencing this REE stability rather than the presence of magnetite. Higher stability of Ce can be ascribed to the possibility of isomorphic substitution of Fe or Fe-O groups by structural Ce on Fe (hydr)oxides (Mohapatra et al. 2005) and the presence of segregated phases as discussed below.

In spite of the similarities between La and Ce, in average, La recovery from precipitates by acetic acid was higher than other REE. It is worth of note that La presents the largest atomic radius among the REE. This can be responsible for a weaker interaction between La and the mineralogical phases precipitated in its presence. Mineralogical phases such as lepidocrocite and gibbsite are admittedly less stable than goethite and magnetite (Lindsay 1979). Our results also suggest that lanthanite is rather unstable relative to Fe (hydr)oxides. On the contrary, segregation of Ce, as cerianite, was highly stable. It is noteworthy that Ce recovery by acetic acid was higher at low Ce contents, but it was quite low at its highest content (500:50 Fe:Ce molar ratio). Therefore, segregation of Ce co-precipitated with Fe (hydr)oxides is highly recommended to avoid environmental risks for disposal of sludge from wastewater treatment. This result also suggests the possibility of REE selective recovery from sludge.

Aluminium seems to impair REE stability in precipitates from La and Nd treatments, but the same was not observed for Ce, Eu and Ho. It can be seen that the presence of Al increased the La recovery rates by acetic acid, irrespective to the Al amount as there were not significant differences between 500:80:5 (La4) and 500:160:5 (La5) Fe:Al:La molar ratios. On the other hand, for Nd, one can observe that treatments with 500:150 (Nd1 and Nd2) were more stable than 150:350 (Nd3 and Nd4) Fe:Al molar ratios (Fig. 17). It can be considered that Al is ubiquitous in tropical environments and even more abundant than Fe in some situations, especially in AMD from alkaline rocks. Then, our results arouse the need for Fe:Al molar ratio adjustment in water treatment to improve the REE stability in precipitates.

In summary, the stability of REE in precipitates is rather controversial. On the one hand, water extractions indicate high stability, but on the other, recoveries by acetic acid suggest low stability of REE in precipitates. Nonetheless, the lack of legal threshold for REE hinder the assessment of environmental risk for disposal of the precipitates. Studies on the health effects of REE are still scarce and controversial when compared to other contaminants, so the levels for adverse effects still need to be stablished (Chen et al. 2015; Li et al. 2013; Wey et al. 2013).

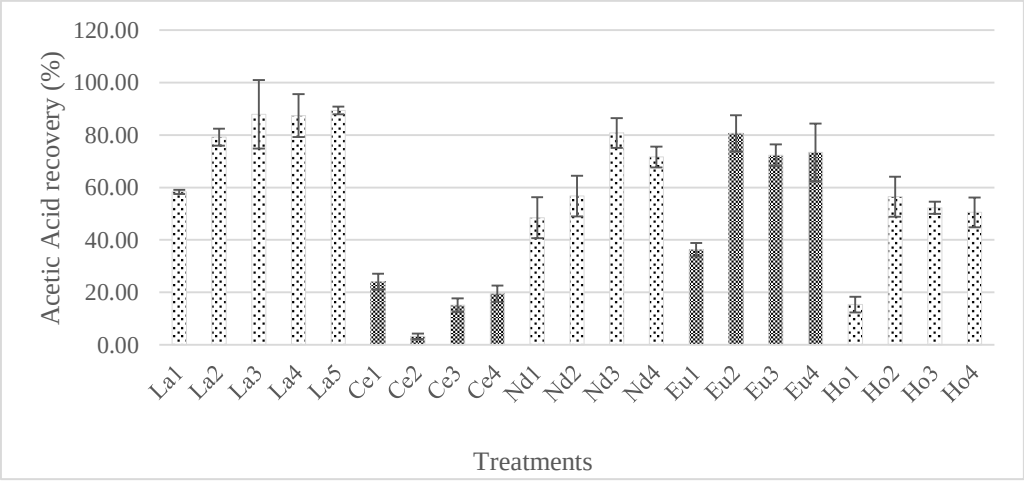

Fig. 17 Recovery of REE from precipitates by acetic acid (0.11 mol L^{-1})

3.3. Immobilization of La, Ce, Eu and Ho from a mixed aqueous solution by co-precipitation with Fe/Al (hydr)oxides from ferrous and ferric sulphates

3.3.1. REE removal from water and mineralogical phases precipitated

Most treatments showed high removal efficiency of REE from water with final concentrations around 0.01 mg L^{-1} for all treatments at pH 9.0 (Table 8). However, treatments at pH 6.0 and Fe(II) showed lower removal efficiency for all REE, especially in the absence of Al (500:0:50 Fe:Al:REE molar ratio).

Treatment Fe(II)_5 (400:100:50 Fe:Al:REE molar ratio at pH 6.0) presented higher REE removal efficiencies than Fe(II)_4 but still much lower than treatments at pH 9.0. This can be ascribed to the higher surface area of treatment Fe(II)_5 (Fig. 18) and then, higher REE sorption by precipitates in the presence of Al due to a decrease in the crystal size favoured by the structural Al as argued by Schwertmann and Cornell (2000). In general, the presence of structural Al provoked an increase in surface area, as expected, at pH 9.0 and 6.0 for Fe(II), but only at pH 9.0 for Fe(III) treatments. Usually, this is related to the mineralogical phases, but in this case, it could not be verified due to the dominance of amorphous phases in precipitates as will be discussed later.

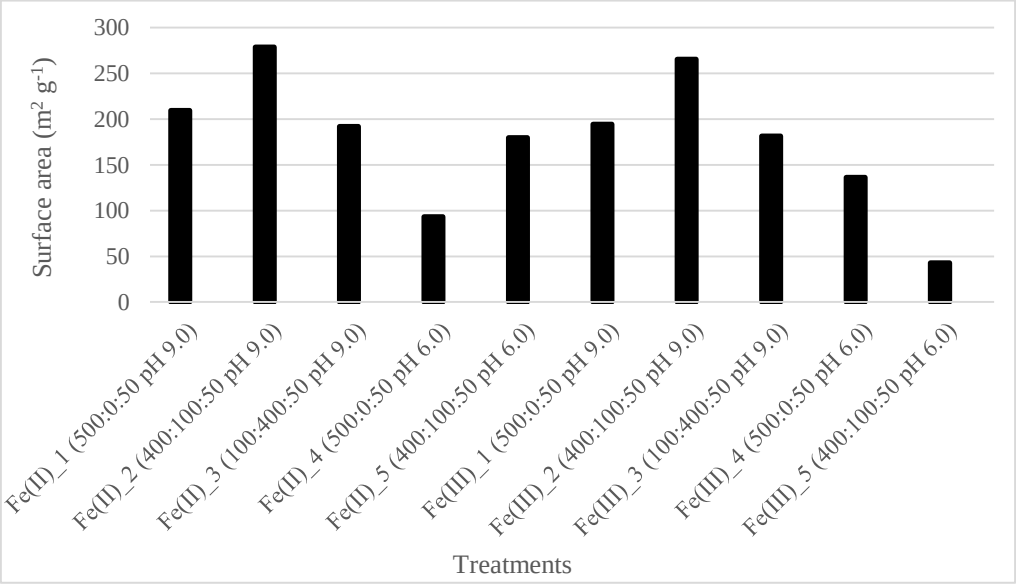

Fig. 18 Surface area of precipitates from different treatments as measured by BET isotherms

Table 7 Initial and final concentrations of REE in supernatants and their removal efficiency from water for different treatments

Treatment	Fe:Al:REE molar ratio	pH	REE Concentrations (mmol L^{-1})								Removal Eficiency (%)			
			La		Ce		Eu		Ho		La	Ce	Eu	Ho
			Ic	Fc	Ic	Fc	Ic	Fc	Ic	Fc				
Fe(II)_1	500:00:50	9.0	1.25	0	1.25	0	1.25	0	1.25	0	100	100	100	100
Fe(II)_2	400:100:50	9.0	1.25	0	1.25	0	1.25	0	1.25	0	100	100	100	100
Fe(II)_3	100:400:50	9.0	1.25	0	1.25	0	1.25	0	1.25	0	100	100	100	100
Fe(II)_4	500:0:50	6.0	1.25	1.01	1.25	1.07	1.25	1.23	1.25	1.18	19	14	2	6
Fe(II)_5	400:100:50	6.0	1.25	0.53	1.25	0.39	1.25	0.21	1.25	0.14	57	69	83	88
Fe(III)_1	500:00:50	9.0	1.25	0	1.25	0	1.25	0	1.25	0	100	100	100	100
Fe(III)_2	400:100:50	9.0	1.25	0	1.25	0	1.25	0	1.25	0	100	100	100	100
Fe(III)_3	100:400:50	9.0	1.25	0	1.25	0	1.25	0	1.25	0	100	100	100	100
Fe(III)_4	500:0:50	6.0	1.25	0.02	1.25	0	1.25	0.01	1.25	0.01	99	100	99	99
Fe(III)_5	400:100:50	6.0	1.25	0.04	1.25	0	1.25	0.02	1.25	0.02	97	100	98	98

Different results were obtained by Barcelos (2014) who observed a high removal efficiency of La from water in the absence of Al. This author obtained a removal efficiency of 97.55% due to co-precipitation of La with Fe(II) (500:0:50 Fe:Al:La molar ratio) at pH 7.5. In the present study, the removal efficiency was just 19% at a higher Fe(II):La ratio (500:0:12.5 Fe:Al:La molar ratio) and lower pH (6.0). Besides the differences in pH's, this comparison reveals the influence of competition among different REE, as that study dealt with a single REE solution compared to a mixed solution in this case. Even though the La concentration was lower in the mixed solution, its removal efficiency was probably impaired due to the competition with other REE.

Another important difference that can be ascribed to the competition among REE is the low crystallinity of precipitates in this study compared to the results from Barcelos (2014). It can be seen that mineralogical phases precipitated were mostly amorphous (Figs. 19 and 20). The main exception was treatment with Fe(II) in the absence of Al (500:0:50 molar ratio) at pH 6.0 that presented comparatively well crystallised goethite peaks. At pH 9.0 one can also recognise poorly crystallised goethite and lepidocrocite precipitated from Fe(II) and hematite from Fe(III) treatments. This is in agreement with Schwertmann and Taylor (1989) who argued that slow oxidation of Fe(II) favours precipitation of goethite, while the presence of ferric ions favours precipitation of hematite.

It is also worth of note that no magnetite peaks were detected in precipitates from Fe(II) treatments, even in the absence of Al. Based on previous studies magnetite should be detected at Fe(II):REE molar ratios higher than 500:50 (Barcelos et al. 2018a, 2018b; Pietralonga et al. 2017). However, in these previous studies individual REE were considered, while a mixed REE solution was used here instead. In the present case, the molar ratios were always 500:12.5 considering individual REE, but the sum of them reached 500:50. Therefore, it seems that the presence of REE prevents precipitation of magnetite at Fe(II)/REE molar ratios equal to lower than 10, considered the sum of all REE.

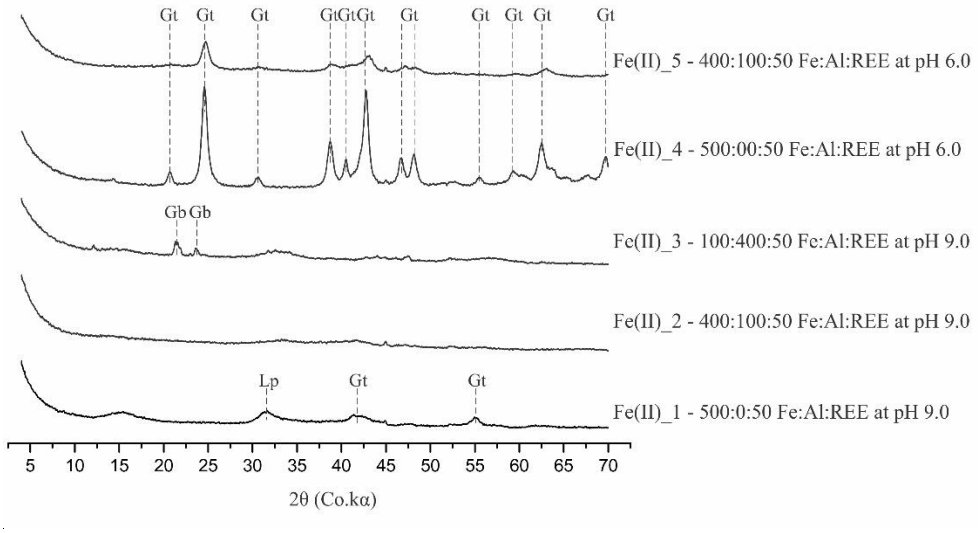

Fig. 19 Diffractograms of precipitates from Fe(II) treatments in the presence of REE (La, Ce, Eu and Ho). Gt – Goethite; Gb – Gibbsite; Lp – Lepidocrocite.

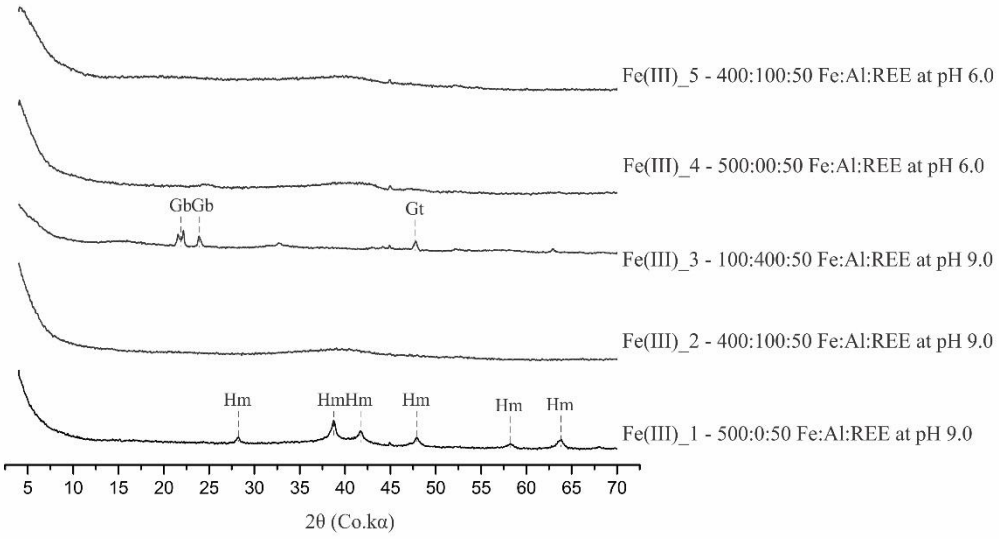

Fig. 20 Diffractograms of precipitates from Fe(III) treatments in the presence of REE (La, Ce, Eu and Ho). Gb – Gibbsite; Gt – Goethite; Hm – Hematite.

SEM micro chemicals maps did not show evidences of LREE segregation (Fig. 21) probably due to the use of lower REE individual concentrations compared to previous studies regarding La and Ce. Molar ratios between Fe and individual REE in the present study was 500:12.5 while studies with La (Pietralonga et al. 2017) and Ce (Cardoso 2014)

had Fe:REE molar ratios up to 500:125 for La and 500:100 for Ce. Then, precipitation of lanthanite and cerianite may have occurred, but in low amounts so it was not detected by SEM analysis.

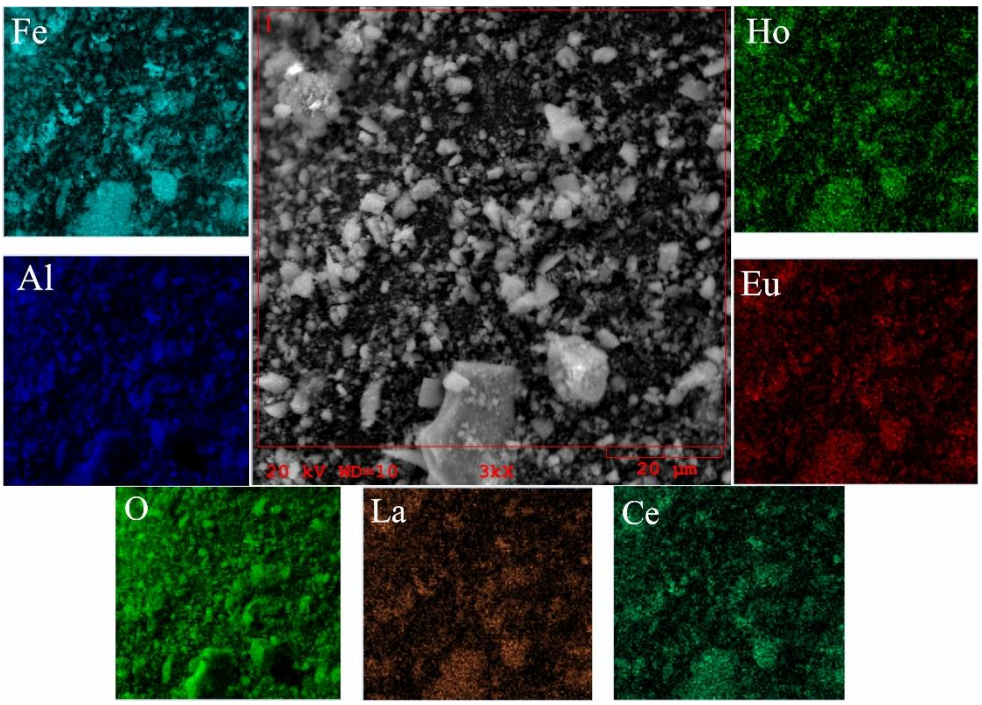

Fig. 21 SEM images of precipitates from treatment Fe(II)_2 (400:100:50 Fe:Al:REE molar ratio at pH 9.0) and microchemical maps for Fe, Al, O, La, Ce, Eu and Ho

As discussed before, treatment with Fe(II) in the absence of Al at pH 6.0 presented the lowest efficiency to remove REE from water. It also presented higher concentrations of soluble Fe over all the incubation period (Fig. 22), indicating that the delay in Fe precipitation impaired the REE removal efficiency from water. In the presence of Al, the Fe(II) precipitation was also delayed at pH 6.0 (400:100:50 molar ratio), but to a lesser extent. In this case, REE removal efficiency was higher than in the absence of Al, but still lower than all other treatments in which Fe precipitated in the beginning of the incubation period. Such results suggest that most of REE removal from water by Fe(II) just takes place after Fe/Al (hydr)oxides precipitation at pH 6.0. On the other hand, the prompt REE removal from water in Fe(II) treatments at pH 9.0 or in Fe(III) treatments at both pH's, favoured precipitation of poorly crystallised Fe/Al (hydr)oxides phases.

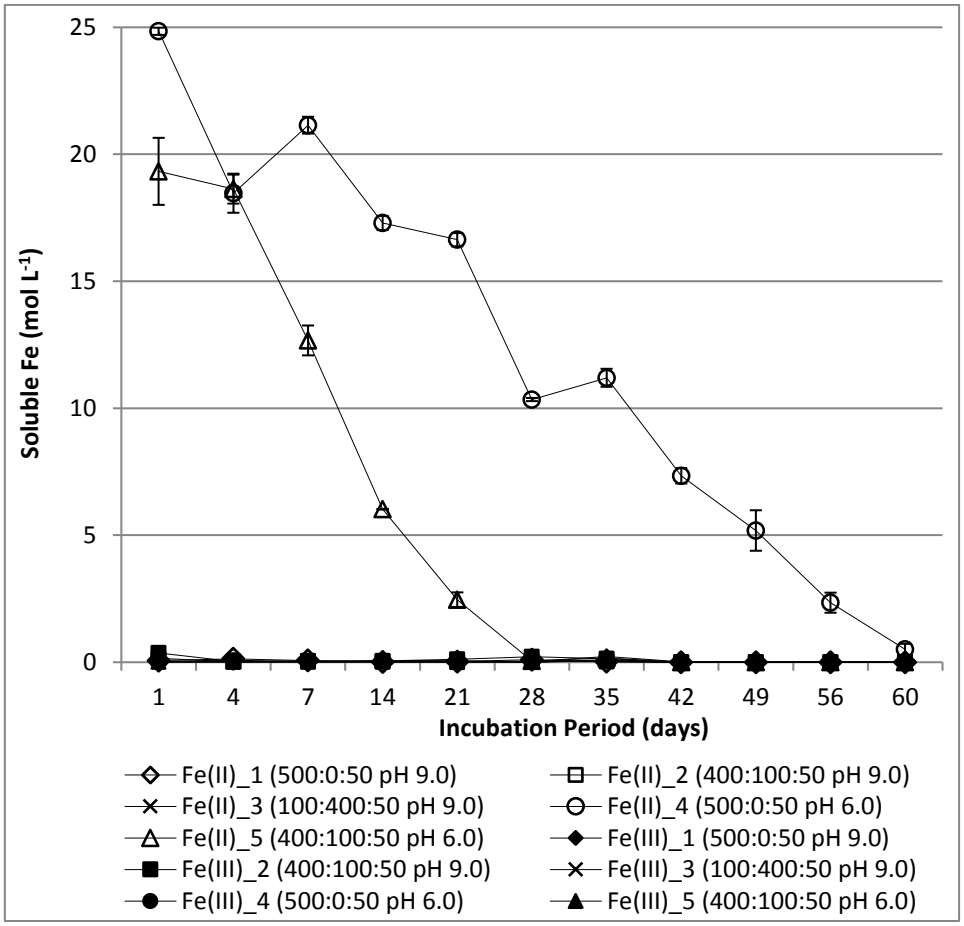

Fig. 22 Concentrations of soluble Fe in supernatants during incubation period

In addition to lower removal efficiencies, treatments with Fe(II) at pH 6.0 also revealed significant differences among REE. The removal efficiencies from water were more than three times higher for light (La and Ce) than for medium (Eu) and heavy (Ho) REE in the absence of Al (500:0:50 Fe:Al:REE molar ratio) (Table 8). In this case, it can be considered that co-precipitation of segregated phases of light REE did occur, although they were not detected by XRD or SEM analyses as previously discussed. Precipitation of lanthanite ($La_2(CO_3)_3.8(H_2O)$) was obtained by Pietralonga et al. (2017) at 500:25 Fe:La, while cerianite (CeO_2) was clearly detected by Barcelos et al. (2018b) at 500:50 Fe:Ce molar ratio. Therefore, it is reasonable to ascribe the higher removal efficiencies of La and Ce to precipitation of lanthanite and cerianite, as segregated phases of Eu and Ho have not been previously reported (Barcelos et al. 2018a). On the other hand, La and Ce presented lower removals from water in treatment Fe(II)_5 (400:100:50 Fe:Al:REE molar ratio at pH 6.0), probably due to the presence of Al (Table 8). It is clear that

structural Al increased the Fe (hydr)oxides surface area in treatments at pH 6.0 (Fig. 18), which probably favoured sorption of Eu and Ho due to their smaller atomic radii relative to La and Ce.

The discussion in the previous paragraphs addresses to the importance of pH on mechanisms of REE sorption by Fe/Al (hydr)oxides. At pH 9.0 the removal efficiencies of REE from water were very high as to overshadow any difference among them. On the other hand, results at pH 6.0 suggest preferential co-precipitation of LREE while MREE and HREE are rather adsorbed. Therefore, it remarks the relevance of ionic radii, surface areas and equilibrium constants on REE adsorption/co-precipitation mechanisms. At higher surface area (400:100:50 Fe:Al:REE molar ratio), the adsorption mechanism prevails favouring Eu and Ho uptake by Fe/Al (hydr)oxides; but at lower surface area (500:0:50 Fe:Al:REE molar ratio), co-precipitation mechanism overcomes, privileging La and Ce removal from water. Indeed, REE partitioning has been observed in estuaries and ocean waters, showing that Fe precipitates not only sequester REE from water, but also fractionate them (De Carlo et al. 2000; Sholkovitz 1995; Martin et al. 1976). According to Bau (1999), such partitioning is due to the differences in REE electron structure. Verplanck et al. (2004) also attested that HREE were preferentially removed from water due to Fe precipitation in AMD at pH 6.1.

It is worth of note that REE removal efficiencies from water were above 97% in Fe(III) treatments even at lower pH (Table 8). This can be related to a prompt Fe precipitation and a more stable pH during the entire experimental period for Fe(III) treatments (Fig. 23). On the contrary, higher pH range was verified in Fe(II) treatments due to oxidation reactions and consequent H^+ release. It is conceivable that pH stability creates a more suitable condition for REE sorption reactions independent on the mechanism involved. The more stable is the system relative to redox dynamics, the stronger is the association between REE and precipitates. Anyhow, this study showed that co-precipitation of Fe/Al (hydr)oxides from both Fe(II) or Fe(III) sulphates can efficiently remove REE from water with final concentrations being very low (Table 8). From a practical perspective for wastewater management, these results point out the possibility of treating AMD at lower pH's in the presence of Fe(III). On the other hand, they suggest the need for Fe(II) oxidation previously to AMD neutralisation to pH 6.0.

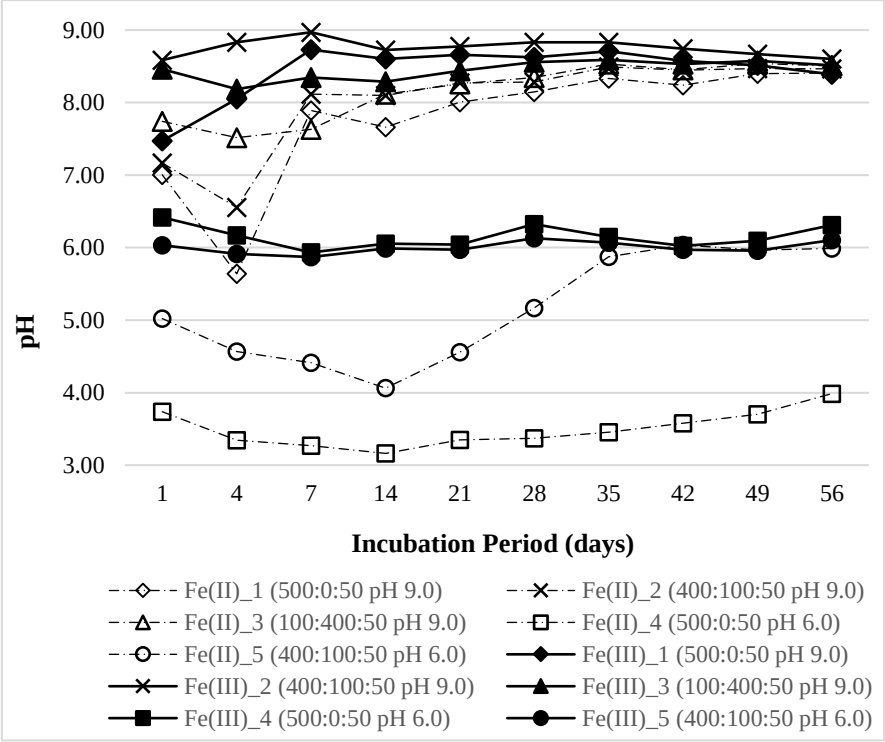

Fig. 23 pH values in supernatants during incubation period

3.3.2. Stability of precipitates

REE recovery percentages from precipitates by the sequential extractions were calculated in relation to the theoretical total contents calculated based on the initial REE concentration in water, the removal percentage from water and the precipitated mass (Table 9). Water-soluble REE phases, determined by sequential washings, were below the detection limit (DL) for all treatments at pH 9.0 (Table 10). However, recoveries were higher in treatments at pH 6.0, especially with Fe(II) in the absence of Al (500:0:50 Fe:Al:REE molar ratio). As previously discussed, these treatments were also less efficient to remove REE from water (Table 7). Then, the results reflect soluble phases that precipitated during oven-drying as the samples were not dialysed previous to washing. On the other hand, treatments with Fe(III) also presented REE water-soluble phases at pH 6.0, but in a lesser extent. In this case, the removal efficiency from water was pretty high, so that the water-soluble phases cannot be completely addressed to

precipitation during oven-drying. Therefore, they should be ascribed to soluble phases co-precipitated with Fe/Al (hydr)oxides and then lower stability of REE in precipitates. By comparing similar Fe(III) treatments at pH's 6.0 and 9.0, there were no great differences in mineralogical phases, in general amorphous, excepted some hematite peaks in the absence of Al at pH 9.0 (Fig. 20). Therefore, the main factor for instability of REE in precipitates was pH rather than mineralogical phases or Fe valence.

Previous studies have shown that the presence of well crystallised Fe (hydr)oxides, especially magnetite, increased the stability of REE in precipitates (Barcelos et al. 2018a, 2018b; Pietralonga et al. 2017). In the present study, however, magnetite was not detected and the presence of goethite and hematite did not significantly affect the stability of REE in precipitates. Therefore, it can be hypothesised that lower pH did not allow a stable association between REE and Fe (hydr)oxides. All studies performed so far with individual REE presented low contents of water soluble phases (usually below DL). Unfortunately, there were no experiences at pH 6.0 in individual REE studies, as to assess the effect of competition among REE on the stability of precipitates.

Results in treatment with Fe(III) at pH 6.0 showed that Ce was much more stable respective to the other REE. On the other hand, La was the least stable as Eu and Ho presented intermediate stability as measured by sequential washings (Table 10). This depict again an important difference between La and Ce in spite of their proximity in the lanthanite series. As lanthanite is more soluble than cerianite, these results also reinforce the hypothesis of La and Ce segregation in precipitates, as discussed before. Barcelos et al. (2018b) also reported lower stability for segregated phases of lanthanite in relation to cerianite co-precipitated with Fe/Al (hydr)oxides.

Table 9 REE total contents in precipitates determined by *acqua regia*

Treatment	Fe:Al:REE molar ratio	pH	Theoretical total content (mg kg^{-1})			
			La	Ce	Eu	Ho
Fe(II)_1	500:00:50	9.0	8560.03	9564.58	10280.20	10700.89
Fe(II)_2	400:100:50	9.0	8979.37	9872.70	10388.73	10749.61
Fe(II)_3	100:400:50	9.0	7098.66	7621.37	5363.66	8679.07
Fe(II)_4	500:00:50	6.0	9725.55	10238.18	10706.40	10981.80
Fe(II)_5	400:100:50	6.0	8962.02	10026.71	11472.79	12155.98
Fe(III)_1	500:00:50	9.0	8660.238	9499.573	10220.28	11282.67
Fe(III)_2	400:100:50	9.0	8909.47	9798.672	10308.97	11539.4
Fe(III)_3	100:400:50	9.0	7315.286	7695.078	8259.326	8615.266
Fe(III)_4	500:00:50	6.0	8961.081	10052.21	10706.75	11757.13
Fe(III)_5	400:100:50	6.0	9894.768	11909.35	12527.08	13413.44

Table 10 REE recoveries percentage by sequential extractions with water

Treatment	Water soluble phases (mg kg^{-1})				Recovery Percentage (%)			
	La	Ce	Eu	Ho	La	Ce	Eu	Ho
Fe(II)_1	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Fe(II)_2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Fe(II)_3	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Fe(II)_4	9024.91	9603.28	10143.75	10072.68	92.80	93.80	94.74	91.72
Fe(II)_5	7029.30	6311.27	4169.74	2982.21	78.43	62.94	36.34	24.53
Fe(III)_1	<DL	<DL	31.05	<DL	<DL	<DL	0.01	<DL
Fe(III)_2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Fe(III)_3	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Fe(III)_4	1346.032	232.28	796.0397	963.1902	29.26	4.50	14.48	15.96
Fe(III)_5	1539.301	192.1438	872.0749	887.4616	31.02	3.22	13.88	13.19

DL_{La}= 0.0042 mg L^{-1}; DL_{Ce}= 0.004 mg L^{-1}; DL_{Eu}= 0.0031 mg L^{-1}; DL_{Ho}= 0.0043 mg L^{-1}

In general, most of the REE in precipitates was removed by acetic acid, excepted Ce, which was mostly extracted by hydroxylamine (Fig. 24). By considering that acetic acid extracts exchangeable phases, as hydroxylamine addresses to reducible phases (Larios et al. 2012), one can state that Ce was rather co-precipitated than adsorbed onto Fe (hydr)oxides surfaces. Similar results were obtained in previous studies and have been ascribed to isomorphic substitution of Fe by structural Ce on Fe (hydr)oxides (Barcelos et al. 2018b; Mohapatra et al. 2005).

At pH 9.0, the presence of Al (400:100 Fe:Al molar ratio) decreased the acid extractable phases of La, Eu and Ho compared to Al absence (500:0 Fe:Al molar ratio) only for Fe(II) treatments. On the other hand, the increase of Al in precipitates, from 400:100 to 100:400 Fe:Al molar ratio, increased the acetic acid extractable phases for both, Fe(II) and Fe(III) treatments (Fig. 24). The role of Al on stability of trace elements associated to Fe (hydr)oxides is rather controversial. There are reports that the presence of Al decreases the stability in precipitates for some REE (Barcelos et al. 2018b; Pietralonga et al. 2017), but not for others (Barcelos et al. 2018a, 2018b). Mello et al. (2018) also observed decreasing As stability in precipitates, while Silva et al. (2010) demonstrated increasing As stability due to the presence of structural Al in Fe (hydr)oxides. All these authors dealt with co-precipitation of trace elements with Fe/Al (hydr)oxides from Fe(II) salts. Vasques et al. (2018), however, did similar studies of As co-precipitation with Fe/Al (hydr)oxides, from both Fe(II) and Fe(III) salts. Their results revealed that Al increases the As stability only in precipitates from Fe(II) treatments. In the present study, it is clear that Al segregation, probably as amorphous $Al(OH)_3$, also decreased the stability of Ce in precipitates from Fe(II) treatments, but structural Al in Fe (hydr)oxides did not significantly affect it. Then, it can be considered that the stability of some trace elements in precipitates increases due to Al isomorphic substitution in Fe (hydr)oxides, but the opposite occurs when segregated phases of Al precipitate as $Al(OH)_3$.

Some REE extracted by hydrogen peroxide were detected, but it probably have no meaning in terms of oxidisable phases. The same was observed by Mello et al. (2018) who discarded the occurrence of oxidisable phases as ferrous compounds or sulphides in a similar experiment with sulphates salts. The occurrence of such phases was also considered unlikely in the present study because they should be limited to treatments with Fe(II), but the contents of hydrogen peroxide extractable REE were, in general, higher in precipitates from Fe(III) treatments. Then, these results can be addressed to remaining REE from previous extractions, other than oxidisable phases. It can be considered that sequential extractions methods are rather operationally defined and the steps did not necessarily address to the target phases (Keon et al. 2001; Rauret et al. 1999). Readsorption of remaining phases from one step and subsequent desorption in the next

step can be a serious limitation for sequential extractions procedures (Baig et al. 2009; Wenzel et al. 2001).

In general, total REE contents recovered by sequential BCR extractions in treatments with Fe(II) are above 75%, excepted for the treatment with 400:100 Fe(II):Al molar ratio at pH 9.0 (Fig. 24). On the other hand, recoveries from treatments with Fe(III) are around 50%, excepted for the treatment with 100:400:50 Fe(III):Al molar ratio at pH 9.0 that is at almost 75% for all REE. All these results point out to a high potential for recovery of these elements from the sludge of wastewater treatment depending on the economic viability and the Fe source. It is worth of note that similar studies with As indicate that this element cannot be significantly extracted from precipitates by BCR procedure. This is interesting as it suggests safe recovery of commercially valuable REE from wastewater even in the presence of highly toxic As.

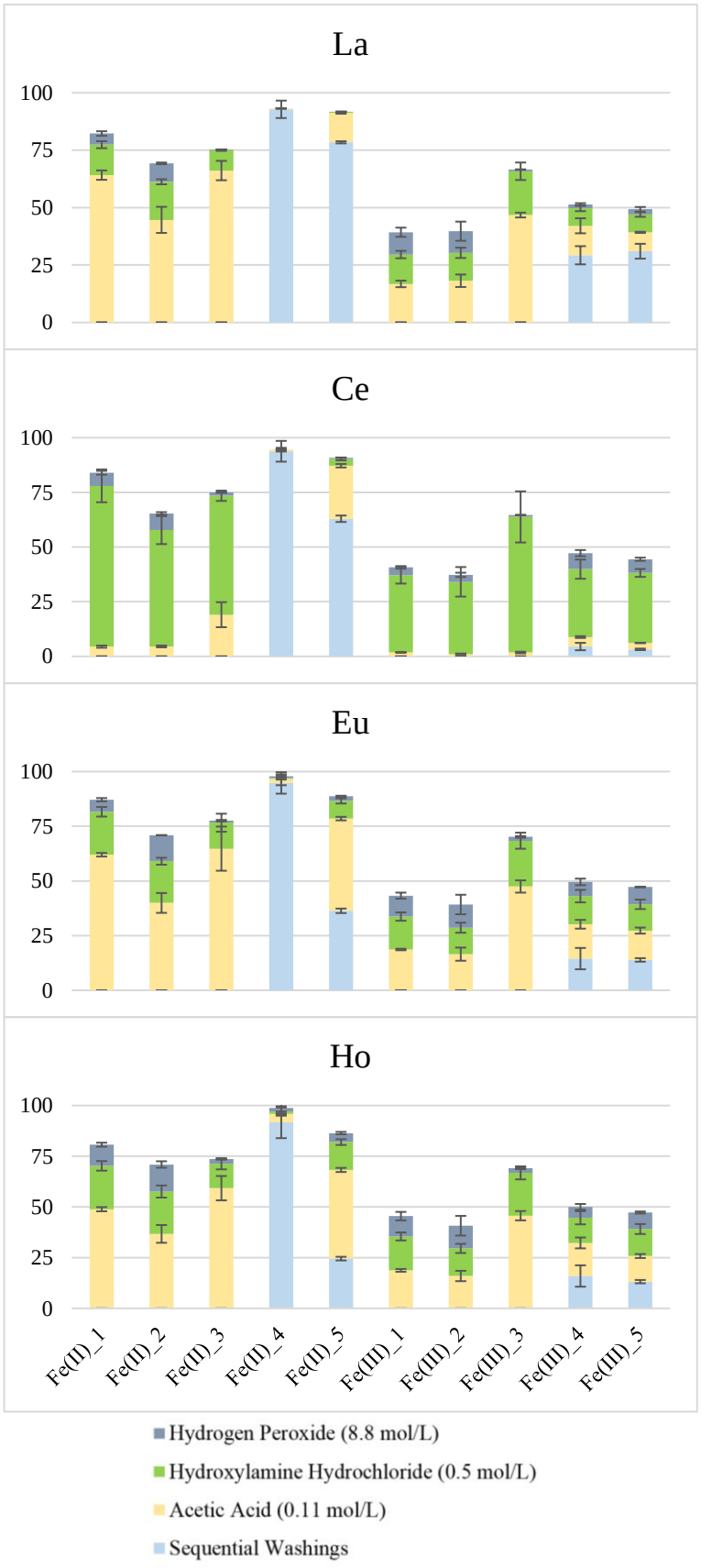

Fig. 24 REE recoveries from precipitates by BCR sequential extractions

The sum of BCR extractions, excepted water soluble phases, depict an interesting scenario when individual REE recoveries are considered (Fig. 25). It can be seen that all REE presented similar recoveries from precipitates, especially in treatments at pH 9.0. On the other hand, at pH 6.0 there were differences among REE. In treatments with Fe(II), recoveries of La and Ce were lower than Eu and Ho, but in treatments with Fe(III), recovery of La was the lowest while Ce presented the highest recovery, both at pH 6.0. Such results reveal the possibility of REE separation from precipitates based on the pH and iron valence in water treatment.

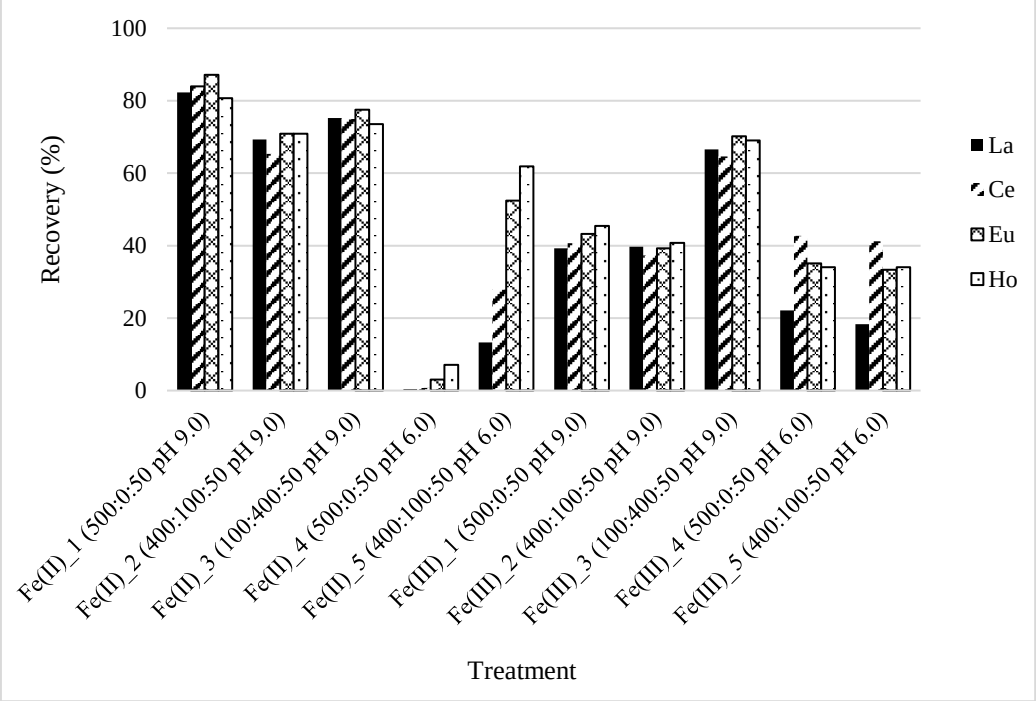

Fig. 25 Total REE recoveries from precipitates by BCR sequential extractions, excepted water soluble phases

This is the first study on using co-precipitation of REE with iron (hydr)oxides to treat water contaminated with a mixed REE solution and it is feasible to consider that the results were satisfactory. It can be useful for REE recovery from AMD treatment in real situations with advantages over passive treatments.

4. Conclusions

- Precipitation of Fe and Al (hydr)oxides presented high remotion for treatment of water contaminated with europium and holmium independently of the molar ratios Fe:Al:REE in the range from 500:0:5 to 400:100:25.

-The higher was Eu and Ho concentrations in water, the higher was their recovery from Fe/Al (hydr)oxides precipitates by BCR sequential extractions. These analyses showed higher amounts of REE solubilized by acetic acid leaching, but the recovery of Eu was superior to Ho.

- Magnetite was the dominant phase in the absence of Al and at lower REE contents. Increasing Al and REE contents favoured goethite, and gibbsite was also detected at higher Al contents.

- High REE contents also favoured precipitation of lepidocrocite in detriment of magnetite, except for Ce and Ho. Magnetite was the main mineralogical phase even at higher Ce and Ho contents.

- Segregated phases were detected at high contents of La and Ce at pH 11.7, as lanthanite and cerianite, respectively. On the contrary, segregated phases were not detected at higher contents of Nd, Eu and Ho at pH 9.0.

- Water soluble phases of REE were not significant, but acid leaching revealed low stability of these elements in precipitates. Furthermore, the stability of REE co-precipitated with Fe/Al (hydr)oxides was related to the mineralogical phases in precipitates. The presence of magnetite favoured the stability of REE, whereas co-precipitation with lepidocrocite and gibbsite impaired their stability in precipitates.

- Segregation of REE co-precipitated with Fe/Al (hydr)oxides provoked opposite effects on stability of La and Ce. Precipitation of cerianite provided higher stability, whereas lanthanite occurrence impaired the stability of precipitates.

- The present study also assessed the influence of pH, Fe valence and Fe:Al molar ratio on treatment of water containing a mixed REE solution. Results revealed that the REE removal efficiency from water was mainly affected by pH and Fe valence. The efficiency was very high for all treatments at pH 9.0 for both, Fe(II) and Fe(III), but

significantly lower at pH 6.0 for Fe(II) treatments. This imply that REE contaminated water can be efficiently treated by co-precipitation of Fe/Al (hydr)oxides from Fe(III) sources at pH 6.0 to 9.0.

- Prompt co-precipitation of REE with Fe/Al (hydr)oxides from both, Fe(II) and Fe(III) at pH 9.0, and from Fe(III) at pH 6.0, produced typically amorphous solid phases. On the other hand, the delay in Fe(II) oxidation at pH 6.0 resulted in well crystallised phases, lower REE removal efficiency from water and high contents of water soluble REE in precipitates. Notwithstanding, the presence of goethite and hematite in some treatments did not significantly affect the stability of REE in precipitates.

- The dominant REE phases in precipitates from treatment of a mixed REE solution, as assessed by BCR sequential analyses, were the acetic acid extractable. Considering the sum of BCR extractable phases, there were no considerable differences and Fe valence did not affect the stabilities of REE in precipitates for treatments at pH 9.0.

FINAL REMARKS

The experiment performed in this study aimed to evaluate options for treatment of water contaminated with REE by Fe/Al (hydr)oxides co-precipitation. The results revealed that is possible to concentrate these elements from wastewater just by adjusting the suitable Fe:Al:REE molar ratio. Treatments presented high REE removal efficiency from water containing individual REE independently on the Fe:Al:REE molar ratios. Results from the study with mixed REE solution, revealed that the water treatment efficiency was mainly affected by pH and Fe valence. All treatments at pH 9.0 were efficient independent on Fe valence or Fe:Al molar ratio, but Fe(II) treatments were considerably less efficient at pH 6.0. From a practical perspective for wastewater management, these results point out the possibility of treating AMD at lower pH's in the presence of Fe(III) or the need for iron oxidation in the presence of ferrous sources.

Competition among REE in a mixed solution revealed differences in removal efficiencies at pH 6.0. Delay in Fe(II) oxidation at pH 6.0 resulted in well crystallised phases, lower REE removal efficiency from water and high contents of water soluble REE in precipitates. This suggests that most of REE removal from water by just takes place after Fe(II) oxidation and consequent Fe/Al (hydr)oxides precipitation at pH 6.0. On the other hand, the prompt REE removal from water treated with Fe(II) at pH 9.0 or with Fe(III) at both pH's, favoured precipitation of poorly crystallised Fe/Al (hydr)oxides phases.

Magnetite was the dominant phase in the absence of Al and at lower REE contents. Increasing Al and REE contents favoured goethite, and gibbsite was also detected at higher Al contents. High REE contents also favoured precipitation of lepidocrocite in detriment of magnetite, except for Ce and Ho. The presence of magnetite favoured the stability of REE, whereas co-precipitation with lepidocrocite and gibbsite impaired their stability in precipitates.

Lanthanite and cerianite segregated phases were detected at high contents of La and Ce, respectively. On the contrary, segregated phases were not detected at higher contents of Nd, Eu and Ho. The occurrence of REE segregation caused opposite effects

in the stability of precipitated phases. Cerianite provided higher stability, whereas lanthanite impaired the stability of these REE in precipitates.

This was the first study on using co-precipitation of REE with Fe/Al (hydr)oxides to treat water contaminated with a mixed REE solution and it is feasible to consider that the results were satisfactory. It can be useful for REE recovery from AMD treatment in real situations with advantages over passive treatments, in terms of costs and length of the procedure. The possibility of REE recovery from the sludge of wastewater treatment is another important point to consider. This could positively affect the total cost of wastewater treatment, depending on the possibility of REE commercialisation.

Results of this study revealed important differences between La and Ce in spite of their resemblances. Therefore, future studies should explore differences in stability among REE, aiming to separate each other from water treatment sludge. Such processes need to be further understood as the REE are strongly related and difficult to be isolated from common sources due to their chemical similarities.

It is worth of note that the occurrence of poorly crystallised phases in precipitates seemed to be stimulated due to competition among different REE. These mineralogical phases also seemed to interfere in the efficiency of water treatment. Then, further studies on the influence of Fe/Al (hydr)oxides crystallisation process are also need. They could start through inducing crystallisation of the amorphous phases obtained in this study.

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